1987

Gallium-Arsenide Film Formation From Low Temperature Chloroaluminate Melts.

Steven Paul Wicelinski
Louisiana State University and Agricultural & Mechanical College

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GaAs film formation from low temperature chloroaluminate melts

Wicelinski, Steven Paul, Ph.D.
The Louisiana State University and Agricultural and Mechanical Col., 1987
GaAs FILM FORMATION FROM LOW TEMPERATURE CHLOROALUMINATE MELTS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemistry

by

Steven Paul Wicelinski
B.S., Fairfield University, 1981
August 1987
For Mom and Dad,

and

To the memory of Babci and Dziadzi
ACKNOWLEDGEMENTS

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ABSTRACT

Prospects of electrochemically forming layers of the III-V semiconductor GaAs from room temperature chloroaluminate melts (AlCl$_3$:1-butylpyridinium chloride (BPC) or AlCl$_3$:1-methyl-3-ethylimidazolium chloride (MEIC)) are investigated. Prior to codeposition experiments, electrochemical behaviors of gallium and arsenic species were investigated by voltammetry, potentiometry and coulometry, and the complexation discussed in acid-base terms. At room temperature, deposition of Ga(0) was possible from acidic but not basic melts, whereas deposition of As(0) was achieved from acidic, basic and neutral melts. Potentiometry of Ga(I) species as a function of melt acidity indicates that GaCl$_2^-$ may be the predominant lower valence gallium species in the basic regime. Little dependence of Ga(I) was found on melt acidity in acidic chloroaluminate melt compositions. Fast atom bombardment (FAB) mass spectrometric analyses of chloroaluminate melts, with and without added GaCl$_3$ or AsCl$_3$, are reported. Anions such as AlCl$_4^-$, Al$_2$Cl$_7^-$, GaCl$_4^-$ and Ga$_2$Cl$_7^-$ were detected along with subvalent species. In addition, various oxychloro and hydroxychloro species such as Al$_2$OCl$_5^-$, AlCl$_3$OH$^-$,
Al$_2$Cl$_6$OH$^-$ and Al$_3$Cl$_8$O$^-$, along with the corresponding Ga species were detected. Results obtained reflect the chemistry in the condensed phase as well as gas phase reaction products.

Potentiostatically controlled reduction of mixtures of Ga(III) and As(III) in acidic AlCl$_3$:BPC and neutral AlCl$_3$:MEIC melts lead to films containing both gallium and arsenic. When both Ga(III) and As(III) are present in acidic AlCl$_3$:BPC melts, with Ga(III) in excess, electrodeposits are obtained which contain crystalline GaAs. Electrodeposited films were analyzed by X-ray Fluorescence, Electron Dispersive Scattering, Inductively Coupled Plasma and X-ray Diffraction.

Mixtures of GaCl$_3$ and BPC or MEIC were found to constitute a novel room temperature melt system. Differential Scanning Calorimetry, Electrochemical, FAB Mass Spectrometric and Raman studies were performed to characterize these melts. The suitability of these melts for thin film fabrication of GaAs is discussed briefly.
1.1 A NEED FOR ALTERNATIVE ENERGY SOURCES

Especially since the November 1973 Oil Crisis, caused by the Arab Embargo on the export of crude oil to the United States, it has been realized that the future of conventional energy sources is uncertain. Major studies of energy resources and production indicate that the era of dependence on fossil fuel is rapidly coming to an end. Even with efficient use of current fossil fuels, increasing energy demands will require a diversification of energy sources. From a global perspective, if mankind desires to maintain or ameliorate its present standard of living, renewable energy sources need to be developed as soon as possible.

Currently, United States' energy demands are met through the use of fossil fuels such as crude oil, natural gas and coal. In addition, nuclear and hydro-power assist in meeting a small portion of the energy needs (Table I). Though coal, petroleum and natural gas presently account for a large percentage of our energy demands, coal is the only fossil fuel expected to be in abundance over the next few hundred years. Without a doubt, reliance on large coal reserves for energy
Table I. Estimates of United States Energy Input for 1984

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>Coal ($10^{12}$ Btu)</th>
<th>Natural Gas ($10^{12}$ Btu)</th>
<th>Petroleum ($10^{12}$ Btu)</th>
<th>Hydroelectric ($10^{12}$ Btu)</th>
<th>Nuclear ($10^{12}$ Btu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>129</td>
<td>2,600</td>
<td>1,173</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Electric Utilities</td>
<td>13,958</td>
<td>3,220</td>
<td>1,286</td>
<td>3,741</td>
<td>3,539</td>
</tr>
<tr>
<td>Transportation</td>
<td>---</td>
<td>545</td>
<td>19,295</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>All Consumers$^a$</td>
<td>17,012</td>
<td>18,504</td>
<td>31,052</td>
<td>3,750</td>
<td>3,540</td>
</tr>
</tbody>
</table>

$^a$ All Consumers = Residential + Commercial + Industrial + Transportation
production would not be prudent, and development of renewable energy sources would allow the conservation of fossil fuels for certain products that are not available from other sources. The potential energy contribution of nuclear power, once considered the energy alternative of the future, is being severely restricted because of limited availability of high grade uranium and prohibitive economic costs. At the present time, the exploitation of solar energy appears to be the best option to alleviate the impending energy dilemma.

1.2 UTILIZATION OF SOLAR ENERGY

Solar energy is a resource which is abundant and environmentally clean. Eventually, solar power could be the primary and, conceptually at least, the exclusive source of heat, electricity, and synthetic fuels for the entire world. To utilize solar energy, research must be directed toward finding ways to efficiently convert the energy of sunlight into a more useful form. Techniques that use the high inherent energy of the visible light photons offer the most promise. The best known of such techniques is photovoltaic conversion. Electricity can be generated directly from sunlight by taking advantage of a phenomenon known as the photovoltaic effect. The
photovoltaic effect may be defined as the generation of electromotive force produced from the absorption of ionizing radiation. Solar cells utilize sunlight to generate a voltage using the photovoltaic effect. Since they consume no chemicals, have no moving parts, and require no maintenance, solar cells are one of the simplest power sources in existence. In addition, they are modular, compatible to almost all environments and have no inherent lifetime limit. Basically, solar cells possess a lifetime limit dependent on material stability and system corrosivity. Several commercial photovoltaic systems are ready for use in a multiplicity of applications and can make a significant contribution to energy demands before the year 2000. However, these systems require further research and development to make them cost competitive for energy production. The cost of electricity from solar cells has decreased by a factor of ten during the past decade and there does seem to be justification for the view that it may approach one dollar a watt by 1990. Photovoltaic cells, of a type used during the past two decades to generate electricity in space, have recently been used in megawatt demonstration projects generating electricity during 30% of the time they were in place. However, before the photovoltaic technologies can become competitive in the
marketplace, further progress must be made on the semiconductor materials technologies involved. Cells demonstrating the best performance of the photovoltaic effect, in terms of being the most efficient converters of sunlight into electricity, utilize semiconductor materials.

1.3 SEMICONDUCTOR PHOTOVOLTAIC CELLS

Semiconductors are materials with electrical conductivities between those of metals ($\sim 10^5$ mho/cm) and those of insulators ($\sim 10^{-5}$ mho/cm). Their electrical conductivities increase exponentially with temperature and exhibit sensitivity towards crystal perfection, frequency of applied electric fields, pressure, sample purity, and temperature. For example, the introduction of an electrically active impurity can increase the electrical conductivity of a semiconductor by several orders of magnitude. In general, the electrical properties of materials are related to the valence electrons which in semiconductors form localized chemical bonds of covalent or somewhat ionic character. At absolute zero, the valence electrons in a semiconductor are bonded completely and no conduction may occur. Bond strength and temperature usually determine whether or not the
electrons can enter the conduction band and become available for conduction. Besides the effect of temperature, the energy gap of a semiconductor influences the conductivity of a particular material. Energy regions for which no electron energy states are allowed are called energy gaps. The energy gap, \( E_g \), which is related to the bond strength, represents the energy required to excite an electron from its bonded state to its conducting state (Table II). Thus, the smaller the energy gap, the greater the concentration of electrons in the conduction band at a particular temperature. For semiconductors, the energy gap lies in the range of 0.1 to 2 eV. In general, the band gap increases as the tendency for electrons to become localized on atoms increases.

The laws of quantum mechanics dictate how electrons will occupy the individual energy levels within an energy band. Utilization of the Fermi function, \( f(E) \), which gives the probability of an electron level with energy \( E \) being filled, best describes the distribution of electrons within the allowed levels:

\[
f(E) = \left(1 + \exp\left(\frac{E - E_F}{kT}\right)\right)^{-1}
\]

(1)

In the Fermi function, \( E_F \) is the chemical potential of the electrons in the system, \( k \) is Boltzmann's constant.
Table II. Properties of Common Semiconductors (25°C)

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Eg (eV)</th>
<th>Electron Mobility (cm²/V·s)</th>
<th>Hole Mobility (cm²/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge</td>
<td>0.76</td>
<td>3800</td>
<td>1820</td>
</tr>
<tr>
<td>Si</td>
<td>1.11</td>
<td>1900</td>
<td>500</td>
</tr>
<tr>
<td>SiC(β)</td>
<td>2.3</td>
<td>4000</td>
<td>---</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.58</td>
<td>540</td>
<td>28</td>
</tr>
<tr>
<td>InP</td>
<td>1.27</td>
<td>4600</td>
<td>150</td>
</tr>
<tr>
<td>GaP</td>
<td>2.24</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.35</td>
<td>8800</td>
<td>400</td>
</tr>
</tbody>
</table>
and $T$ is the absolute temperature. When the energy gap is overcome in a semiconductor, electrons are excited into the conduction band and conduction is then possible. After the excitation of an electron to the conduction band, an electron deficiency in the valence band known as a hole results. Thus, for every electron in the conduction band there exists a hole in the valence band. In an applied electromagnetic field, both the electrons and holes may move and contribute to the electrical conductivity of the semiconductor. Basically, a hole acts as a unit positive charge. Semiconductors which meet the preceding description fall into the category of intrinsic semiconductors. The electrical conductivity of a pure undoped semiconductor is usually referred to as the intrinsic conductivity.

Chemical impurities or crystal defects can cause an excess, or a deficiency of electrons, upsetting the exact balance of electrons and holes. When this situation occurs, the semiconductor is classified as an extrinsic doped semiconductor. If an excess of electrons are present, they cannot be accommodated in the valence band and, consequently, enter the conducting band. There are more electrons than holes and the conductivity is primarily due to the electrons. Since it is customary to
classify a semiconductor according to the sign of its majority carriers, a semiconductor with an excess of negatively charged carriers is labelled as n-type. When an excess of holes exists in the valence band, there exists a deficiency of electrons. Therefore, the conductivity is primarily due to the holes which are positively charged carriers. A semiconductor which possesses an excess of positive charge carriers is labelled as p-type. As mentioned previously, impurities may have a significant effect on the electrical conductivity of a semiconductor, e.g., the addition of one boron atom per hundred thousand silicon atoms produces a threefold increase in its conductivity at room temperature. Impurities are referred to as donors if they yield an electron to the conduction band or acceptors if a hole is formed in the valence band. Quite common is the process of introducing one of the Group III or V elements into Si or Ge. Present semiconductor technology is making good use of the extreme sensitivity of semiconductors to particular impurities. Properly doped materials are utilized in the fabrication of crystal diodes, integrated circuits, photodetectors and transistors.

Photovoltaic devices comprise semiconductor materials that transform solar energy into direct current
electricity. Their basic principle of operation is the interaction between photons and electrons. When a n-type semiconductor is placed in contact with a p-type semiconductor, conduction electrons from the n-region diffuse across the junction into the p-region and combine with holes. An opposite action also occurs with holes from the p-region crossing into the n-region and combining with electrons. Thus, the diffusion of electrons and holes across the interface produces a local region with an electric field. This electric field allows free electrons to move one way while the free holes move in the opposite direction. When light falls on the device surface, photons with energies greater than the bandgap interact with the valence electrons and promote them into the conduction band. Consequently, electron-hole pairs are generated throughout the semiconductor materials. Those pairs which reach the junction are separated by the pre-existing electric field, with a potential difference being established across the device. If a connection were made between the n and p-type semiconductors via an external circuit, current would flow through the circuit to reduce the built up charge imbalance. Continuous illumination creates a sustained supply of electron-hole pairs, thereby, allowing the device to drive a current through the external circuit.
1.4 METHODS OF SEMICONDUCTOR DEPOSITION

Before photovoltaic technologies can become competitive in the marketplace, further progress must be made to the semiconductor materials technologies involved, especially in the cost of materials preparation and device fabrication. In addition, the conduction of electricity in photovoltaic devices depends on reproducible interfaces between metallic conductors and good quality semiconductor materials. Closely related is the development of an understanding of the mechanistic chemistry and physics that affects device efficiencies.⁹

A variety of methods have been employed to deposit thin films of semiconductor materials on a number of possible substrates. Some of the more common methods include:

1) Evaporation,
2) Liquid phase epitaxy (LPE),
3) Sputtering,
4) Molecular beam epitaxy (MBE),
5) Chemical vapor deposition (CVD), and
6) Electrodeposition.

Evaporation may be classified as the simplest vacuum deposition process in the electronics industry. When a
particular source material is heated under vacuum to an appropriate temperature, a significant amount of evaporation occurs. The vapor from the source material will travel until it condenses onto a selected substrate producing a thin film. It is extremely important to maintain an ultra-high vacuum during the process, otherwise the vapor produced from the source material may collide with the background gas molecules causing an inefficient deposition of the substrate. Resistive heating is used in most cases of vacuum evaporation. The substrate material is usually supported by a filament or crucible of refractory material which does not react with the substrate vapor. Since crucibles and filaments have finite vapor pressures, care must be taken to avoid contamination of the film.

Liquid phase epitaxy involves the growth of an epitaxial layer on a single crystal substrate. Growth occurs by deposition from a molten solution saturated at the growth interface. The basis of this process is the decreasing solubility of a dilute component in a liquid solvent with decreasing temperature. When a saturated solution in contact with a single crystal substrate is cooled properly, epitaxial deposition of a thin film occurs on the substrate. This process yields layers of
accurately controlled composition and thickness by controlling the solution composition, cooling process, and substrate orientation. With precise control of the system parameters, high quality films can be produced. However, it is difficult to obtain uniformity of alloy composition and doping in the growth direction. In addition, liquid phase epitaxy layers do not have as good surface morphology as layers grown by vapor phase epitaxy.

Sputtering is a process in which energetic projectile particles bombard a target and physically eject atoms from a target surface. Ejected atoms then enter the surrounding vacuum and travel through the system until they condense on a suitable substrate. This technique is well suited for the growth of alloys and compounds whose elemental components possess widely varying melting points and vapor pressures. Semiconducting films can be grown with essentially any desired composition or spatial variation in composition. Since there exists a decrease in yield with increasing atomic mass of the target material, deposited films are rich in the most easily sputtered component. Though sputtering offers tremendous versatility in the growth of semiconducting films, it has a few disadvantages. In general,
film growth rates during sputter deposition are often lower than with other techniques. Also, the relatively high background gas pressures often found in sputtering systems may cause contamination in deposited films. These difficulties may be minimized by utilizing techniques such as substrate biasing or ion beam sputtering, but even these techniques have their own limitations.

Molecular beam epitaxy utilizes neutral, thermal, molecular or atomic beams which strike a heated substrate in an ultrahigh vacuum system. Several furnaces with different elements or compounds are maintained at appropriate temperatures to produce a sufficient vapor pressure. At high enough vapor pressures, the desired beam flux is produced at the surface of the heated substrate. The thermally generated beams must be produced in such a way that their composition and intensities remain constant. Since the growth temperature is relatively low, undesirable thermally activated processes such as diffusion are minimized. With a relatively slow growth rate, molecular beam epitaxy is capable of achieving atomically smooth surfaces. Another advantage is its flexibility to incorporate a variety of source beams. However, it suffers from a failure to achieve the high degree of purity and perfection that semiconductor films require.
These difficulties should be overcome with further progress in ultrahigh vacuum technology.

Chemical vapor deposition, a purely chemical vacuum process, involves a gas phase reaction which results in the formation of an epitaxial film. The process involves pumping down a vacuum system to low pressure and then introducing the appropriate reactive gases in the presence of a buffer gas. Once the mixed gases react, they form a non-volatile semiconducting material which then deposits onto a selected substrate. Various temperature zones are involved and temperature gradients must be carefully controlled. Compound semiconductor films can be prepared by a process known as metal organic chemical vapor deposition (MOCVD). This growth process involves the thermal decomposition of volatile organometallic transport agents to deposit thin films. With respect to the deposition of III-V semiconductors, Group III alkyls and Group V hydrides are typically used as transport agents. For example, the deposition reaction to produce GaAs is:

$$\text{Ga(CH}_3\text{)}_3 + \text{AsH}_3 \rightarrow \text{GaAs} + 3\text{CH}_4$$  \hspace{1cm} (2)

MOCVD is a nonequilibrium process which can be used to produce complex materials whose constituents may differ
in heats of formation. Proper operational care must be taken to avoid premature decomposition of the Lewis acid-base adducts. Though MOCVD can be used to selectively deposit thin films of a variety of desired materials, it uses starting materials that are flammable, pyrophoric, or toxic, and appropriate precautions must be taken. In general, CVD systems use chemical transport, thermal decomposition and reduction to deposit doped and undoped semiconducting films. Similar to MBE, CVD techniques waste a large quantity of expensive raw material. To overcome this drawback an expensive recycling of unused raw materials is required.

Electrodeposition, a process with an electrochemical driving force, is capable of precise control in the production of semiconductor materials. The applied voltage at an appropriate electrode substrate provides the driving force for the deposition of a desired material. Passage of current by ionic conduction in the cell is the result of a net oxidation-reduction reaction in which electrochemically active species are reduced at the cathode and oxidized at the anode. Deposition reactions occur when the electrode potential exceeds the decomposition potential for the crystallizing species. An excess potential is used to drive the kinetic processes at the
electrodes. Electrodeposition may occur at constant current (galvanostatic control) or at constant potential (potentiostatic control). The process is a relatively low temperature technique that avoids thermal decomposition and high vapor pressures. Electrodeposition is an isothermal process and does not require the establishment and maintenance of temperature gradients. Since the technique is relatively temperature insensitive, small temperature changes do not affect the growth rate. Another advantage of electrodeposition is that in certain cases it may be possible to control the epitaxy of electrodeposited films while introducing dopants into the material. One of the most important advantages of electrodeposition is that very accurate control of deposition may be obtained by the ability to precisely control the electrochemical parameters. This precision may be orders of magnitudes greater than that possible for thermal parameters.

1.5 MOLTEN SALT ELECTROCHEMICAL TECHNIQUES

Without a doubt electrodeposition offers more potential advantages for certain semiconductor materials growth than the previously mentioned techniques. Though aqueous systems can usually be employed for metals
deposition, nonaqueous systems are chemically more appropriate for semiconductor deposition in the important cases of Si and the III-V materials. Nonaqueous media include organic solvents, inorganic solvents such as Lewis acid halides, oxyhalides, etc., and molten ionic electrolytes. Since the development of the Hall process for refining aluminum in the 1930's, the applications for molten salt electrochemistry have exhibited a slow but steady evolution. Some of the current interests in molten salt methods center on the development of inexpensive processes to electrowin and/or deposit large area films of silicon and compound semiconductors. This interest could result in the development of economical solar cell production techniques. With respect to semiconductor deposition, molten salt electrochemical techniques offer the prospects of being relatively inexpensive and scalable to industrial production.

Electrowinning and -refining are two important processes in molten salt chemistry. Electrowinning is a procedure by which metals are recovered by electrolysis from an appropriate solution and electrorefining is an electrolytic process for the subsequent removal of impurities. The metallurgical importance of Al electrowinning is apparent from the fact that all the commercial
aluminum is produced in this manner. Electrolysis of aluminum oxide in molten cryolite, using a carbon anode and a molten aluminum cathode, produces commercial grade Al. Studies to develop processes to electrowin and/or electrorefine semiconductor-grade silicon have been undertaken. \textsuperscript{12} Using a ternary mixture of LiF-NaF-KF (FLINAK) at 745°C with at least 4\% of K$_2$SiF$_6$, Rao et al. have been able to electrowin Si. \textsuperscript{13} Electrolysis produced coherent, well-adhered films on Ag substrates in thicknesses up to 3\,mm using c.d.s in the range 10-60 mA/cm$^2$. Kibbler et al. investigated the prospects of using a Si-Cu anode in a molten fluoride to examine an electrorefining process for purifying metallurgical grade Si. \textsuperscript{14} Impurity levels and electrical properties were determined with the results showing promise for electrorefining processes in semiconductor materials production. Olson and Carleton have developed a semipermeable anode that enhances the effectiveness of the electrorefining process and permits the low temperature fabrication of Si anode plates. \textsuperscript{15} Using a K$_2$SiF$_6$ electrolyte, by refining with a high c.d., high purity graphite cathode and a Si-Cu anode, they improved by twofold the purity of deposited Si compared to previous work. Monnier and coworkers performed extensive studies on achieving Si refining simultaneously with electrodeposition. \textsuperscript{16,17} Their most
promising results were produced from a silicon oxide/cryolite melt at 1000°C, with efficiencies to 85% and purity as high as 99.99%.

1.6 ELECTRODEPOSITION OF SEMICONDUCTOR MATERIALS FROM MOLTEN SALTS

Before the advent of silicon based semiconductor devices, germanium based devices were preeminent in the semiconductor industry. Though the electrodeposition of Ge is no longer of much technological interest, early deposition studies employed molten cryolite and molten carbonates as solvents and generally GeO₂ as the solute. Barbier-Andrieux deposited Ge using various molten borate, fluoride, phosphate and silicate systems. Typical electrolyses were performed at currents of 10-20 A, with potentials greater than those needed for deposition being employed, with a crucible made of graphite as the cathode and a graphite anode. Purities as high as 99.9% were achieved from a GeO₂-Na₂O-NaF system at 1000°C with 51% current efficiency. Further investigations using molten fluoride melts were performed by Monnier and Tissot, who obtained Ge deposits of 99.9% purity at temperatures below the melting point of Ge with current efficiencies approaching 50%. Rius and coworkers
obtained Ge deposits of 99.99% purity using molten borate systems at 1100°C. Current efficiencies were low and investigations under similar conditions employing silicate melts yielded deposits of lower purity.

With the decline of Ge based devices, Si based devices became of major importance. The first reported electrodeposition of Si is credited to Deville. However, the first systematic study of Si electrodeposition is credited to Dodero who electrolyzed alkali metal and alkaline earth silicates at temperatures between 800 and 1250°C. Sodium and potassium silicates with the corresponding fluorides at temperatures in excess of 1100°C yielded the best quality of electrodeposited Si. Though the purity was only slightly greater than seventy percent, his work laid the foundation for future breakthroughs.

Cohen and Huggins produced coherent epitaxial and polycrystalline layers of Si using a molten system at 760°C containing 5 mol % K2SiF6, 10 mol % KHF2, and 85 mol % LiF-KF. Their melts were purified by pre-electrolysis, after which deposition was performed utilizing a high purity anode and various substrates as the cathode. Improved growth rate and layer morphology were obtained using an alternating square wave pulse.
technique. Using a high quality single crystal substrate formed of Ge or Si, Cohen has been able to electrodeposit epitaxial crystal layers. This process involves using the substrate as the cathode with the minimum concentration of the plating ion salt being 0.1%, at 600-850°C, and c.d.s in the range 1-20 mA/cm².

Researchers have found that the most successful deposition of Si thus achieved is from a eutectic mixture of LiF-KF with 8-14 mol % of K₂SiF₆. Deposition may be performed at either constant current or potential with c.d.s usually less than 100 mA/cm². Rao and coworkers have found the best c.d.s typically to range from 15-30 mA/cm² with current efficiencies approaching slightly better than 80%. The highest purity of Si electrodeposited from a molten salt system was obtained by Elwell and coworkers, who obtained Si of better than 99.999% purity on graphite substrates from a K₂SiF₆-LiF-KF melt at 745°C. Recently, Si was electroplated at 750°C from alkali metal fluorides containing K₂SiF₆. The deposits grew three dimensionally from nuclei formed simultaneously, with the structure of the plate being voltage dependent. In addition, Si has been electrodeposited above its melting point from a BaO-BaF₂ melt containing SiO₂. Lump-like deposits up to 15mm in
diameter and 99.9% purity were obtained by employing c.d.s as high as 1 A/cm².

Silicon carbide, a wide band gap semiconductor, has presented crystal growers with a formidable challenge. It has been reported that thin layers of epitaxial SiC were electrodeposited onto SiC substrates from lithium carbonate melts at 1000°C containing SiO₂. Although the melt system exhibited good long term stability, attempts to grow bulk crystals were hindered by delamination of the seed crystals. Attempts to electrodeposit SiC from various carbonate/fluoride melts have been less than successful, producing deposits containing excess carbon.

Electrodeposition studies of the most common metal chalcogenide semiconductors from molten salts have received much less attention than from aqueous or organic solutions. Markov et al. have electrodeposited CdS from a LiCl-KCl melt containing CdCl₂ and Na₂SO₃. Smooth, thin films were deposited onto Cu and Ag electrodes at 450-500°C and c.d.s 0.2-0.5 mA/cm². Single crystal CdSe modified by the thermodiffusion of Cu from a NaCl-KCl molten system containing CuGaSe has been investigated. Cathodic deposition of CdTe has been achieved from a eutectic mixture of LiCl-KCl at 400-500°C containing TeO₂.
and CdCl$_2$. Electrodeposition of ZnSe and ZnTe from molten salts has been achieved and the authors reported obtaining epitaxial ZnSe deposits on Si substrates from a KCl melt at 550°C containing ZnCl$_2$ and SeCl$_4$. A similar process for the electrodeposition of ZnTe was used but detailed results were not reported. Films of ZnSe also have been electrodeposited from a KCl-LiCl melt at 470°C containing ZnO and Na$_2$SeO$_3$. The films obtained at c.d.s in the range 0.4-3.2 mA/cm$^2$ contained some oxide impurities but were the best quality ZnSe films obtained thus far.

Electrochemical deposition of thin films of CuSe has been achieved from a melt containing CuCl$_2$, SeO$_2$ and LiCl at 550°C. Using an oxidized Al cathode and a graphite anode, with c.d.s 5-15 mA/cm$^2$, uniform films having semiconductor properties were obtained. Further attempts have been made to obtain CuSe films on an oxidized Al surface by electrodeposition, but at lower temperatures. Treatment of the Al cathode by electrochemical polishing and electro-oxidation prior to deposition reportedly improves the film quality and further investigations are ongoing.
Anodization in molten salt electrolytes to prepare semiconductor films has been shown to be feasible. Hirata et al. have anodically oxidized Ti in molten NaNO$_3$ containing Na$_2$O$_2$ at 315°C. Photocurrent, photovoltage, and capacitance measurements showed these films to consist of a p-i-n junction. Abdullahi et al. have investigated the photoresponse of TiO$_2$ films grown anodically from molten urea-ammonium nitrate mixtures at 63.5°C. They found the photocurrents of films obtained by molten salt anodization to be favorable to thermally grown films. Also, Al has been anodized in molten eutectic nitrate melts at temperatures below 140°C.

The pioneering work on molten salt electrodeposition of III-V compound semiconductors is credited to Cuomo and Gambino, who achieved epitaxial growth of GaP. These deposits were made on both Si and GaP substrates from a melt containing Ga$_2$O$_3$, NaF and NaPO$_3$ at 800°C. The GaP, deposited at 50 mA/cm$^2$, was doped by adding Zn (for p-type) and Se (for n-type). From the same investigations, Cuomo and Gambino reported that AlP and InP could be produced by replacing Ga$_2$O$_3$ by Al$_2$O$_3$ or In$_2$O$_3$ in the metaphosphate melt. However, little experimental data was provided, other than mention of similar methods being utilized.
DeMattei et al. have studied the condition necessary for stable growth of epitaxial GaP layers by molten salt electrodeposition. They reported that the usefulness of silicon as a substrate material was limited due to a thermal expansion mismatch with GaP and its reactivity with the melt. In addition, smooth, coherent GaP layers on a GaP substrate could only be obtained at c.d.s below 20 mA/cm² at 800°C.

Utilizing a NaPO₃-KPO₃-NaF-KF melt containing In₂O₃ at 600-650°C, Elwell et al. have electrodeposited InP. Deposition of epitaxial layers was not possible due to the high viscosity of the melt and low solubility of In₂O₃. However, polycrystalline layers of InP were deposited on Ni and CdS substrates at c.d.s in the range 1-3 mA/cm².

The first reported electrodeposition of GaAs from a molten salt system was achieved by DeMattei and co-workers. Using a B₂O₃-NaF-Ga₂O₃-NaAsO₂ melt, they were able to deposit GaAs on Ni and GaAs substrates at 720-760°C. However, epitaxial layers could only be deposited on GaAs substrates and only to 10um thickness. Recently, Tremillon and coworkers have reported the electrodeposition of GaAs at a relatively low temperature.
Under galvanostatic conditions, deposition was achieved on Au electroplated Ni electrodes from a KGaCl$_4$ melt containing AsI$_3$ at 300°C. Current densities of approximately 0.1 A/cm$^2$ were employed. However, X-ray diffractometry, which confirmed the presence of GaAs, also indicated the presence of As impurities.

Molten salt electrochemistry is an established technology that is just beginning to be seriously considered for semiconductor materials growth. Though a variety of useful materials can be prepared by molten salt electrochemistry, its application to crystal growth has received less attention than other techniques. This is indeed quite surprising when one considers the enormous potential that electrodeposition offers. Especially in the past decade, researchers have begun to realize the unique aspects of electrodeposition along with its potential advantages over conventional crystal processing techniques. More research and development must be performed before this process can be fairly compared to conventional processes.
1.7 EMERGING IMPORTANCE OF GaAs

Currently, Si based devices are important in the semiconductor industry, for diodes, integrated circuits, computer chips, and solar cells. However, there exist many other elemental semiconductors, such as B, C (diamond), Se, Te, and gray Sn. Of closely related importance to the Group IV semiconductors are the Group III-V compounds formed from the combination of the elements As, Al, Sb, Ga, P, and In. Other elements such as Cd and Zn are used in various semiconductor materials. During the past decade in particular, there has been an ever increasing amount of research with Group III-V materials. The special significance of III-V semiconductors is that they extend the range of properties of Ge and Si. Revolutionary advances in the electronics industry have occurred because the range of possible applications for semiconductors is so broad. Extensive studies have centered on the interconversion of electrical and optical energy of the III-V semiconductor materials.

The most important III-V semiconductor is GaAs; it is utilized in microwave integrated circuits that are considered superior to their Si counterparts, and microchips composed of GaAs are not only faster but more
energy efficient than Si chips. For this reason it is finding more use in communications systems and very high speed computers. As well as being utilized in integrated circuits, GaAs is finding applications as a laser or light-emitting diode, for which silicon cannot be utilized.\(^{48}\) Recently, scientists at Varian Associates Incorporated reported the development of GaAs based solar energy cells that can convert over 21% of the available sunlight into electricity.\(^{49}\) These cells are being developed for use in outer space, to provide energy for space vehicles and to extend the operating life of satellites. More efficient solar energy cells of this type will allow maintenance of higher power levels for longer periods of time. In addition, since GaAs cells have nearly twice the heat resistance of similar Si cells, satellites may be placed in higher orbits than currently is possible. It is projected that the market for compound semiconductor devices, such as lasers and field effect transistors for opto-electronic communications, aerospace, and military applications will grow from one billion dollars in 1985 to thirteen billion dollars in 1995, and fifty billion dollars by 2000.\(^{50}\)

In a recent Board on Army Science and Technology (BAST) report, alarm was expressed at the United States'
30

decline as an electronics power, noting that Japan is far ahead in several advanced technological areas. The report further stated that communications gear, missile guidance systems, navigation instruments, and other sensitive devices have come to depend on foreign parts and manufacturing expertise. One acute problem mentioned was the production of GaAs. Not only is there a decline of United States production of GaAs, but there exists a lack of research and development centered on this semiconductor in the United States. Several years ago the Japanese government identified opto-electronics as an important area and supported an intense R&D program to produce GaAs. Today, over three-quarters of the free world's supply of GaAs substrate crystal is produced in Japan. Though American companies still dominate the market in GaAs devices, research efforts need to be increased towards fabrication of this important semiconductor. Without a doubt, the potential applications of GaAs are far reaching and the lack of research efforts of concern.

1.8 RESEARCH GOALS

Since GaAs possesses a high photovoltaic energy conversion efficiency, it is a prime candidate for single
material solar cells. However, current device fabrication techniques waste over 99% of the starting raw materials. Thus, more efficient disposition of materials must be achieved to make these devices economically feasible. Theoretically, electrochemical methods of deposition have the advantage of precise control of layer thicknesses, which would enable economical usage of materials. From a review of the literature, it is evident that molten salt electrodeposition can be utilized to produce a wide range of semiconductor materials. In particular, Tremillon and coworkers demonstrated that GaAs could be electrodeposited at moderate temperatures, but insufficient studies were performed to determine the prospects for better quality deposits.46

Considerable interest has arisen in the past decade in molten salt systems that are liquids at room temperature or below.53,54 Mixtures of aluminum chloride and 1-alkylpyridinium halides or 1,3-dialkylimidazolium chlorides are liquids at ambient room temperatures.55-57 The aprotic nature and the freedom of oxygen, as well as the lower temperature which reduces the problems with volatile arsenic species, all suggest the evaluation of these media for thin film fabrication of compound semiconductors. Utilization of these ionic liquids would
significantly reduce the risks involved in current methods of GaAs preparation, which require the use of pyrophoric, toxic, volatile starting materials. The goals of this research therefore have been:

1. An investigation of the prospects of electrochemically forming layers of GaAs from the AlCl₃:1-butylpyridinium chloride (BPC) and AlCl₃:1-methyl-3-ethylimidazolium chloride (MEIC) room temperature melts. This involves codeposition experiments to determine if GaAs films can be produced electrochemically.

2. A description of the electrochemistry of gallium and arsenic species in AlCl₃:BPC and AlCl₃:MEIC molten salt systems.

3. To determine whether alternative ionic molten salt systems are suitable for GaAs fabrication, e.g., melts based on the addition of GaCl₃ to BPC and/or MEIC. Preparation and characterization of these systems would produce insights into their suitability for thin film fabrication of III-V semiconductors.
2.1 PREPARATION AND MAINTENANCE OF INERT ATMOSPHERE

Since most molten salts show high reactivity towards water and/or oxygen, it is imperative that experiments be conducted within an inert atmosphere. The organic chloroaluminate and chlorogallate melts are particularly sensitive to the presence of both water and oxygen. Even the presence of small quantities of water and/or oxygen will result in significant changes in the chemical properties of these media. When non-aqueous chemistry of this type is to be performed, special attention is necessary to exclude and/or remove moisture from the experimental environment. This is by no means a trivial task, especially when one considers that this work is to be performed in the humid environment of Louisiana. Helpful references are available which provide guidelines and suggestions for dealing with air sensitive materials. 58,59

Preparation of melts along with subsequent electrochemical investigations were performed in a stainless-steel glove box constructed by the LSU machine shop. Figure 1 shows a schematic of the glove box system.
FIGURE 1

Schematic of glove box apparatus.
that was employed. External to the dry box are a double column, oxygen scrubber, moisture removal column and circulating pump. In addition, a cylinder of Ar and a vacuum pump are connected to the glove box for use when needed. Except for brief periods during which materials were being transferred, the antechamber was kept in an evacuated condition. Heavy-duty neoprene dry box gloves (Norton, 0.03 inch thickness) were attached to the glove ports located in the front, central portion of the dry box. Since the gloves are probably the major source of atmospheric contamination, it is imperative to maintain a positive pressure within the box and to monitor carefully the condition of the gloves. Banana plug attachments were added to the glove box by drilling through the wall, inserting the sockets and epoxying. This modification was needed for electrical feedthroughs from the electrochemical instrumentation to the cell inside the glove box.

Initial start-ups involved purging the glove box enclosure with a cylinder of nitrogen to remove as much of the air as possible. Afterwards, traces of oxygen and moisture are removed by circulating the inert gas through the oxygen scrubbers and moisture removal columns, using
a Dayton, one-third horsepower, split-phase motor, recirculating pump. Trace amounts of oxygen were removed by Cu-0803, T 1/8, copper catalyst (Harshaw). Composed of 10% CuO mounted on high activity alumina, the copper catalyst was packed into two, two inch diameter, twenty inch long, glass columns. To make these columns effective oxygen scrubbers, they were wrapped with a flexible, 1 3/4" x 48" heating tape (Cole-Parmer) and heated to approximately 250°C. Control of the heating tapes was achieved by use of a Cole-Parmer, SCR voltage controller. The moisture removal column was packed with silica gel and several intermittent layers of Indicating Drierite. In addition, a Drierite column was placed inside the glove box, on-line with the recirculation unit, to aid in moisture removal. Connections between the various valves and components of the recirculation system were made with heavy-duty, vacuum tubing (3/16" I.D.) or thick wall, Tygon tubing (1/4" I.D.).

Continual removal of moisture and oxygen from the internal atmosphere was achieved by continuous recycling. The need for a continuous recirculating purification system arises because of various sources of impurity introduction. These sources include: 1) bringing new
materials into the box via the antechamber, 2) diffusion through the gloves (minimized by positive pressure), and 3) leakage through gaskets and seals. Before addition of an inert gas to the box, it was passed through the oxygen scrubbers and moisture removal columns before entering the main chamber of the glove box.

Periodically, the columns for oxygen and moisture removal required regeneration. To regenerate the oxygen removal columns a slow stream of hydrogen, drawn from an attached cylinder, was passed through the columns at approximately 250°C. The hydrogen gas, vented to the hood, reduced the CuO on the Harshaw catalyst to metallic copper, with the product water vapor exiting with the gas stream. Removal of water from the silica gel/Drierite column was achieved by heating the column to approximately 175°C for several hours under vacuum. Periodically, the internal Drierite column was removed and regenerated outside the glove box.

Nitrogen is the most popular inert gas for glove boxes due to its lower cost in comparison to helium and argon. One of the rare occasions that nitrogen should not be employed is for experiments with Li. During periods of high inert gas consumption, i.e. start-up and
extensive material transfer, nitrogen was used. However, argon was usually the inert gas of choice. Since argon is heavier than air and diffuses much slower than nitrogen, it provided greater protection against atmospheric contamination.

2.2 CHEMICALS, METALS AND SOLVENTS

Acetonitrile - (B.P. 81.6°C) Since the major use of acetonitrile is for the purification of BPC and MEIC, good quality, dry acetonitrile is essential. Aldrich, 99% pure acetonitrile was dried by shaking with Linde, 4A molecular sieves. To remove any traces of water or acetic acid (common impurity), the acetonitrile then was stirred with calcium hydride and fractionally distilled. Storage over molecular sieves helped to exclude moisture from this solvent.

Aluminum - High purity aluminum wire (Aesar, 99.999% purity) was used in the construction of reference electrodes, in the purification of aluminum chloride and in the pre-electrolysis of acidic chloroaluminate melts. The wire, 1.0 mm diameter, was rinsed with acetone, quickly dipped in nitric acid, rinsed with distilled water and dried in the oven before use.
Aluminum Chloride - (Sublimes at 190°C, 2.5 atm) A method of purification of aluminum chloride by sublimation, similar to that of Gale and Osteryoung, was utilized. Fluka A.G. brand aluminum chloride (anhydrous, 99+%) purity) is the only brand which is recommended. Other less pure brands of aluminum chloride increase the risk of explosion when following the procedure below. In addition, the Fluka brand contains only 0.008% (max) Fe, a major contaminant of commercial aluminum chloride.

Thick-walled glass tubes with a male 40/50 joint attached to thick-walled glass tubes with a female 40/50 joint and a #2 stopcock were used for the purification. Approximately 2-5 grams of NaCl, several pieces of Al wire and enough AlCl₃ to half fill the 12" glass tube with the male joint were added. After attaching the respective glass tubes, they were clamped to a ring stand, placed in the hood, and wrapped with a heating tape. The sealed tube then was evacuated for one hour and the heating tape was connected to a voltage regulator. Next, the stopcock was closed and the temperature slowly raised to liquify the contents. Since heating to about 200°C causes a significant build-up of pressure, the purification must be performed behind a safety shield...
with intermittent pressure releases. This can be done by opening the stopcock for a few seconds and evacuating. Once the contents had become molten, the heating tape was gradually lowered to allow sublimation on the upper portion of the tube. After several hours when about 80% of the AlCl₃ has sublimed, heating is ceased and the tube is allowed to cool. The upper phase contains a white-to-clear layer of AlCl₃, while the lower phase contains impurities entrapped within a layer of NaAl₂Cl₇. Finally, the tube is transferred into the glove box, the sublimed product is removed, and it is stored in glass stoppered jars for later use.

**Arsenic Trichloride** - (M.P. 130.2°C, d = 2.163 g/ml)
Sealed ampoules of 99.999% purity were purchased from Aesar and used as received. The clear, colorless liquid was transferred to 25 ml volumetric flasks with ground glass stoppers and sealed with Parafilm until needed.

**1-Butylpyridinium Chloride** - (M.P. 131.5°C) Preparation of BPC was achieved by following the method of Gale et al. with a few minor changes. Equimolar amounts of chlorobutane and purified pyridine were gently refluxed together for about 48 hours. To minimize the moisture exposure of the mixture, a drying tube containing
Drierite was attached to the top of the reflux condenser. After allowing the reaction to go to about 80% completion, the heating mantle was removed and the product was allowed to cool. The product, an off white solid, was separated from the excess reactants and dissolved in a minimum amount of acetonitrile. After the addition of decolorizing charcoal and refluxing for 25 minutes, the mixture was then filtered. Filtration was performed with a pre-heated Buchner funnel, attached to a filter flask containing 10% by volume ethyl acetate. After suction filtration, the contents of the filter flask were allowed to cool while the white BPC crystals formed. During this time the filter flask was tightly stoppered and a drying tube was attached to the side arm to minimize moisture exposure. After several hours of cooling, the excess solvent was removed and the recrystallization process repeated. Depending on the color of the crystals, the recrystallization process was performed 4-5 times with the charcoal being omitted on the final purification. Lastly, excess solvent was removed from the crystals and the crystals were quickly transferred to a vacuum oven. After approximately one day at 65-75°C in a vacuum oven, the BPC crystals were transferred to the glove box and
placed in brown glass jars. The BPC prepared in this manner had a melting range of 131-133°C.

**1-Chlorobutane** - (B.P. 78.4°C, d = 0.886 g/ml) Since chlorobutane does not possess a significant affinity for water and contains no troublesome impurities, Sargent-Welch brand (99+% purity) was stored over molecular sieves and used directly.

**Ethyl Acetate** - (B.P 77.1°C) Utilized during the recrystallization of BPC and MEIC, good quality, dry ethyl acetate is essential in obtaining the high purity organic salts required for electrochemical investigations. Aldrich (99.5+% purity) ethyl acetate was first dried with MgSO₄ and then with P₂O₅ before distillation. The solvent was collected and stored over molecular sieves until needed.

**Ethyl Chloride** - (B.P. 12.2°C, d = 0.897 g/ml) Gas cylinders of ethyl chloride were obtained from Linde. Used in the preparation of MEIC, the ethyl chloride was condensed prior to mixing with 1-methylimidazole. It was inadvisable to obtain ethyl chloride from a cylinder which was less than one-quarter full due to the increased moisture content. In addition, it is helpful to pass the
gas through a column of silica gel and a drying tube containing $P_2O_5$ prior to condensation.

**Gallium** - (M.P. 29.8°C) Ingots of gallium metal of 99.99% purity were obtained from Alfa. Since metallic gallium readily forms an oxide layer, fresh pieces were cut and placed in the well of L-shaped electrodes. Next, the metal was gently melted to wet the glass and form a smooth surface. Gallium working electrodes prepared in this manner were quickly transferred into the glove box and used for various electrochemical investigations.

**Gallium Trichloride** - (M.P. 77.9°C) Crystalline, anhydrous gallium trichloride of 99.999% purity was obtained from Aesar in sealed ampoules and used as received. The high-purity crystals were stored in weighing bottles with ground glass joints and sealed with Parafilm. Due to the corrosive nature of gallium trichloride, it was stored and placed in contact with glass only. Not only are the vapors corrosive to Al foil, but prolonged contact of the vapors with non-glass or non-teflon materials produces impurities which eventually contaminate the high-purity crystals.
1-Methylimidazole - (B.P. 198°C, d = 1.030 g/ml)

Used in the synthesis of MEIC, methylimidazole of 99% purity, obtained from Aldrich, was distilled prior to use. Purification is achieved by vacuum distillation at 55°C over BaO (drying agent) followed by collection and storage over molecular sieves.

1-Methyl-3-ethylimidazolium Chloride - (M.P. 84°C)

Synthesis of the MEIC was performed according to the method developed at the Seiler Research Laboratory. After adding about 150 ml of freshly distilled 1-methylimidazole to a 500 ml glass pressure bottle, an equal amount of ethyl chloride was added. The ethyl chloride is liquefied by passing the gas at about 5-10 psi through a dry ice condenser and into the pressure vessel. Once the appropriate amount of ethyl chloride was added a high pressure clamp was placed over the neoprene stopper. Next, the vessel is placed in a constant temperature bath regulated at 75°C for 2-5 days. Since heating the vessel causes an internal pressure build-up, a safety shield should be placed between the bath and the researcher. After the reaction has proceeded for 2-5 days, the vessel is allowed to cool and the excess reactants discarded. The MEIC was purified by
recrystallization from acetonitrile/ethyl acetate, with particular attention being paid to limiting moisture exposure. Use of airless flasks and performance of filtration under a dry inert atmosphere greatly reduces the risk of water impurity in the crystals. Final traces of solvent were removed by placing the crystals in a vacuum oven or desiccator for about one day. Lastly, the crystals are quickly transferred to a glove box for storage until needed. The MEIC prepared as above melted in the range of 83-85.5°C.

**Platinum** - High purity platinum wire (99.999%) was obtained from Aesar. The wire of 1.0 mm thickness was used in the preparation of various electrodes. For deposition experiments, platinum foil of 99.99% purity and 0.1 mm thickness was obtained from Aesar and used for electrodes.

**Pyridine** - (B.P. 115.5°C, d = 0.982 g/ml) Purification of pyridine prior to BPC synthesis significantly reduces the BPC purification required. Pyridine of 99+% purity was obtained from Alfa and stored over NaOH prior to purification. Refluxing with NaOH for several hours followed by fractional distillation removed most of the water and other impurities initially present. Collection
and storage of pyridine over NaOH insures dry pyridine for the BPC synthesis.

2.3 PREPARATION OF MELTS

Chloroaluminate Melts - These room temperature molten salts are prepared by weighing the appropriate ratios of AlCl$_3$ (M.W. 133.34 g/mol) and BPC (M.W. 171.67 g/mol) or MEIC (M.W. 146.64 g/mol). In most cases, the BPC or MEIC was weighed inside the electrochemical cell and the AlCl$_3$ was slowly added. The presence of a teflon-coated, magnetic stir bar helped facilitate mixing and reduced local heat build-up. Since the addition of AlCl$_3$ to the organic salt produces an exothermic reaction, care was taken to avoid thermal decomposition by careful, gradual mixing. In general, MEIC melts could be mixed more quickly and with less discoloration occurring than their BPC counterparts. Covering the cell with Al foil during mixing reduced vapor losses of AlCl$_3$ which in turn minimized errors in composition determination. Alternatively, the weighed organic salt inside the cell may be placed on a balance and the aluminum chloride slowly added until the desired composition is reached. This method nullifies the effect of any vapor loss and
allows for more accurate mixing of a desired melt composition. It is common practice to express the composition of a melt in terms of apparent AlCl₃ mole fraction, N, or mole ratio, X. The mole fraction, N, may be expressed as:

\[ N = \frac{\text{mol AlCl}_3}{\text{mol AlCl}_3 + \text{mol RCl}} \]  \hspace{1cm} (3)

where R = BP⁺ or MEI⁺. To express the melt composition in terms of the mole ratio, X, of aluminum chloride to the organic chloride, a simple conversion may be used:

\[ X = \frac{N}{1 - N} \]  \hspace{1cm} (4)

**Chlorogallate Melts** - These room temperature molten salts are prepared by mixing the appropriate amounts of GaCl₃ (M.W. 176.03 g/mol) and BPC or MEIC. After placing a weighed amount of the organic salt in a vial or electrochemical cell, gallium trichloride was slowly added. Similar to the mixing of the chloroaluminate melts, the chlorogallate melts must be gradually mixed to avoid thermal decomposition. Unless an external cooling source is provided, special care needs to be taken when combining the respective reagents to prevent excessive heat build-up. In addition, it was found that mixing too quickly in cells covered with Al foil caused
embrittlement of the Al foil. Gallium and its volatile halides rapidly diffuse through the crystal lattices of most metals and are thus quite corrosive. Thus, the mixing and containment of these melts should be performed within the confines of glass or teflon receptacles.

N.B. - All weighings were performed in the glove box using a Mettler P160 Balance. This balance had a maximum capacity of 160 grams and an uncertainty of ± 0.5 mg.

2.4 DESIGN OF THE ELECTROCHEMICAL CELL

All electrochemical cells require at least two electrodes, the anode and the cathode, at which the oxidation and reduction reactions occur, respectively. The electrodes may be connected to a potentiostat/galvanostat for dynamic measurements. However, in this case, a third electrode is required and the system is classified as the conventional three electrode system. The three electrodes for potential/current measurements are a counter, reference and working electrode. A counter electrode (also called an auxiliary or secondary electrode) serves as an electron sink/source, completing the circuit with the working electrode. To measure or control the potential of the working electrode, a stable
reference is required. The reference electrode ideally is a reversible, non-polarizable half cell at which the potential remains constant. Lastly, the electrode under investigation is the working electrode.

Figure 2 illustrates a typical electrochemical cell used for electrochemical investigations. Cells were made of Pyrex glass, with approximate volumes of 25-75 ml (depending on the particular application), and a Teflon lid. Openings were drilled through the lid to allow the respective electrodes to be held in place. The cells were either placed on a magnetic stirrer or placed inside a tube furnace depending on the melt composition and/or the investigation. Tube furnaces were constructed from nichrome wire coiled within and wrapped by asbestos tape in a cylindrical fashion. Next, the assembly was placed within a glass beaker or a vermiculite insulated metal canister. Temperatures were maintained to within ±1°C by an Omega (Model 20M) solid-state temperature controller with a deviation meter and a 0-300°C range. An iron-constantan (Type J), teflon insulated thermocouple was used in conjunction with the temperature controller. For best results and to minimize introduction of
FIGURE 2

Typical three-electrode cell arrangement.
impurities into the melt, the thermocouple was placed between the Pyrex cell and inner wall of the tube furnace.

A glassy carbon counter electrode (A = 1.6 cm$^2$) was used for most of the electrochemical investigations. It was constructed by wrapping nichrome wire around one end of a piece of glassy carbon and attached with silver epoxy. Occasionally, a bent T-shaped piece of Mo foil (A = 1.1 cm$^2$) was used as the counter electrode. For coulometric investigations, the counter electrode consisted of a high purity, coiled Al wire immersed in the particular melt composition. The melt was contained within a glass fritted tube to separate it from the bulk melt.

For BPC based chloroaluminate melts, the reference electrode consisted of a high purity, coiled Al wire immersed in a melt of 2:1 composition. The reference electrode for MEIC based chloroaluminate melts consisted of a high purity, coiled Al wire immersed in a melt of 1.5:1 composition. In both cases, the melts were contained within glass fritted tubes with fine porosity glass frits. Since the purity and composition of the reference electrode could not be compromised, the level
of the reference melt was always kept above the liquid level of the bulk melt. This insured that the reference melt diffused into the bulk melt and not vice versa. Throughout this work all potentials have been quoted with respect to the above reference electrodes depending on the organic salt involved. Potentials between the reference electrode and the working electrode were measured with a Kiethley (179 TRMS) digital voltmeter. The Kiethley meter is a high impedance voltmeter capable of a four decimal place readout, that minimizes current flow between the reference and working electrodes.

Various types of working electrodes were used for electrochemical investigations. Electrodes constructed from Pt wire and sealed in Pyrex glass exhibited the best overall response. Most voltammetric investigations were performed with Pt button electrodes \((A = 0.810 \text{ mm}^2)\). In addition, vitreous carbon \((A = 3.14 \text{ mm}^2)\) and tungsten \((A = 7.06 \text{ mm}^2)\) electrodes were used as working electrodes. Similar to the Pt electrodes, the W and C electrodes were prepared by sealing the respective materials in Pyrex glass. Prior to use, all working electrodes were polished to a mirror like finish using fine alumina (Type B). Next, they were rinsed with distilled water, wiped
dry and further buffed on a fine polishing cloth. Afterwards, they were rinsed in distilled water, washed with acetone, dried and immediately transferred into the glove box.

2.5 ANALYTICAL AND ELECTROCHEMICAL TECHNIQUES

Constant Current Coulometry - This technique requires a knowledge of the current and the time to determine the number of coulombs. In constant current coulometry, the potential of the working electrode is allowed to vary in order to maintain the specified current. The primary electrochemical reaction is an oxidation, or reduction, to produce a desired reagent or chemical species. With a constant current, $i$, and a known period of time, $t$, the number of coulombs passed during an electrolysis can be determined,

$$Q'(\text{coulombs}) = i \cdot t \ (\text{ampere - seconds}) \quad (5)$$

This technique was used to generate electrochemically aluminum and gallium species for various investigations. A Sargent (Model IV) coulometric current source or a Brinkman (E524) coulostat were employed. The following
relationship can be used to determine the quantity of a species generated,

\[ G = \frac{(M)(i)(t)}{(n)(F)} \]  \hspace{1cm} (6)

where: \( G \) is the weight of the generated species, \( M \) is the molecular weight, \( n \) is the valency change and \( F \) is Faraday's constant. Both the Sargent coulometric current source and the Brinkman coulostat have simplified matters by providing an indication of the microequivalents involved.

**Controlled Potential Coulometry** - This coulometric method involves maintaining the potential of the working electrode at a constant value with respect to the reference electrode. Selection of a suitable potential is made from cyclic voltammetry data. Electroactive species were added to a melt contained within a vitreous C or Pt cell, which also served as the working electrode. The electroactive species is depleted during the course of the electrolysis and the number of coulombs used is measured by current-time integration,

\[ Q = \int_{0}^{t} i \, dt \]  \hspace{1cm} (7)
At the commencement of electrolysis, both the concentration of the electroactive species and the current is high. As the electroactive species is depleted with time the current will progressively decay. The current time relationship for a diffusion limited reaction may be expressed as,

\[ i = i_0 \exp(-k t) \]

(8)

where: \( i_0 \) is the initial current, \( k \) is a constant dependent on the cell/electrode geometry and the diffusion coefficient of the species, and \( t \) is the time of electrolysis. Controlled potential coulometric investigations were performed with a PAR 173 Potentiostat/Galvanostat equipped with a PAR 179 Digital Coulometer or an EG&G 273 Potentiostat/Galvanostat. Both instruments were capable of automatic integration of the current with high accuracy and good reproducibility. Though short electrolysis times are desirable, investigations lasting up to 48 hours were easily accommodated because of the low drift in the coulometers of the respective instruments. Working electrode cells consisted of a Pt crucible with a maximum melt capacity of about 15 ml and a C crucible which could accommodate about 50 ml of melt. Counter and reference electrodes were similar to those
previously described in this Chapter. Electrolyses were usually with stirred melts containing less than 150 mg of electroactive species.

**Cyclic Voltammetry** - Examination of the kinetics of electrode processes is achieved by this electrochemical technique. It is a very important tool for the study of oxidation/reduction processes and related chemical mechanisms. Cyclic voltammetry is the measurement of current-voltage curves at a suitable working electrode under diffusion-controlled, mass transfer conditions.

Qualitative analyses were performed by observing the following characteristics of electroactive species: peak potentials, peak shapes, and effects of varying the composition of different low temperature melts. Theoretically, for a reversible redox system where the oxidized and reduced species are soluble, the current will pass through a maximum at a potential, $E_p$, where

$$E_p = E_{1/2} - [(1.1 \ R \ T)/(n \ F)]$$

$E_{1/2}$ is the half-wave potential, $R$ is the gas constant (J/mol K), $T$ is the absolute temperature, $n$ is the number of electrons per molecule oxidized or reduced, and $F$ is Faraday's constant. The peak current, $i_p$, for a
reversible system may be expressed by the Randles-Sevcik equation,

$$ip = (2.69 \times 10^5)n^{3/2} A D^{1/2} v^{1/2} C$$

(10)

where:  $n$ is the number of electrons transferred, $A$ is the area of the electrode, $D$ is the diffusion coefficient, $v$ is the scan rate, and $C$ is the concentration of the electroactive species. Since not all systems are reversible and behave as above more complicated mathematical models must be used for analysis.

Cyclic voltammograms were obtained with a PAR (Model 173) Potentiostat and a PAR (Model 175) Universal Programmer, or a PINE RDE 3 Potentiostat, using a platinum, tungsten or carbon working electrode. Voltammograms were recorded on a PAR 9002A X-Y recorder. The counter electrode usually was glassy carbon. Between 25-250 mg of the species to be studied was added to an appropriate melt, which was maintained at a constant temperature throughout the investigation.

**Differential Pulse Polarography** - In differential pulse polarography, a linear voltage ramp is combined with pulses of a fixed magnitude. Two current measurements are made, one prior to applying the pulse and one
near the end of the pulse, with the first current being subtracted from the second current electronically. Thus, the differential pulse polarogram is a difference in current per pulse recorded as a function of the linearly increased voltage.

Analyses of product films formed on electrodes were made by differential pulse polarography. Polarograms were obtained with a PAR (Model 174A) Polarographic Analyzer and a PAR 9002A X-Y recorder. Samples were prepared by dissolving the film in hydrochloric or nitric acid, diluting to the ppm range with distilled water, and adding to the polarographic cell with an appropriate supporting electrolyte. For the determination of arsenic, 1M HCl was the recommended supporting electrolyte. In the case of gallium, 1M NaSCN was used as the supporting electrolyte. A dropping mercury electrode with a 1-2 sec drop time and a 2-5 mv/sec scan rate is suitable. Trace levels of gallium were confirmed by the attainment of a peak potential at -0.83V vs. a Ag/AgCl/KCl reference electrode. In the case of arsenic, a peak at -0.42V vs. SCE is most sensitive and generally used for quantitation.
**Differential Scanning Calorimetry (DSC)** - This method involves subjecting a sample and a reference substance to a continuously increasing temperature. Thermal energy is added or subtracted from the sample, or reference container (depending on the reaction involved), in order to maintain the two at identical temperatures. The energy input is equivalent to the heat gained, or lost, as a consequence of an endothermic or exothermic reaction occurring in the sample.

Melting points or glass transitions, along with overall thermal stability, were determined for the chlorogallate melts using a Perkin Elmer, Series 7, Thermal Analysis System. This system consisted of a Perkin Elmer (DSC-7) Differential Scanning Calorimeter, a Perkin Elmer (7500) Professional Computer, a Perkin Elmer (TAC 7) Instrument Controller and a Perkin Elmer Graphics Plotter. Samples were contained in stainless-steel pans which were loaded in a glove box with 10-30 mg of melt, carefully placed in the center of the pan. After sealing the sample pans, they were stored in the glove box until required for analyses. The DSC head was purged with Ar at 35-150 cc/min. Each sample was scanned from -65°C to 125°C at a fixed rate between 2 and 10°C/min.
Fast Atom Bombardment (FAB) Mass Spectrometry - This lower-energy particle bombardment technique allows for better mass resolution and shorter experiment times. Chloroaluminate and chlorogallate melts were prepared by mixing accurately weighed quantities of the appropriate starting materials. The samples were prepared in a glove box, sealed in vials and placed in a vacuum desiccator for transfer. Each sample (1-2 microliters) was deposited under an argon atmosphere onto a copper probe tip and immediately placed into the insertion lock. Investigations were performed with a Kratos MS 80 RFA, double focussing, forward geometry mass spectrometer fitted with a post acceleration detector. Fast xenon atoms were produced with an Ion-Tech, saddle field, fast atom gun. The fast atom gun was operated at 9 Kev and a constant current of 0.03 mA. High-purity xenon gas (99.995%) was purchased from Liquid Carbonic. Negative ion mode operation of the mass spectrometer was performed with an accelerating voltage of 4 KV, 30 sec/decade scan rate and a resolution of 1000. Data acquisition and processing was performed with DS 90 (version 3.1) software, operated via a MS 80 autoconsole. Calibration of the instrument from m/z 91-1133 was performed with a CsI/glycerol
mixture. In most cases, 10-15 scans were acquired per sample. After obtaining the desired number of scans, the sample was removed and the sample tip dipped in dilute nitric acid, rinsed with distilled water and acetone, and dried before the next experiment.

**Inductively Coupled Plasma (ICP) Emission Spectroscopy** - In this method, the ICP discharge is formed electromagnetically by radio frequency induction coupling of argon, which is easily ionized and relatively unreactive. Induction occurs without electrode contact, in argon flowing upward through a quartz tube inside a copper coil. Occasionally, films and deposits were dissolved in an appropriate acid, diluted with distilled water and introduced as a liquid into a Perkin Elmer ICP-6500 system for analysis. This system, which contained a Perkin Elmer Plasma Power Supply and a Perkin Elmer Plasma Torch Controller, was operated with the assistance of a Perkin Elmer 7300 Professional Computer. The combination of low background and a high signal-to-noise ratio of analyte emission, yielded low detection limits reaching the ppb range. Minimal ionization interferences occur in ICP and because of the high temperature reached in the discharge all samples are
expected to be completely atomized. Simultaneous multi-element analyses were performed to determine the major and minor constituents of films and deposits.

**X-ray Diffraction (XRD)** - This method allows for the identification of crystalline materials from the measurement of the angles of diffraction. Use of the Bragg equation allows one to determine the conditions under which a beam of X-rays will be diffracted from a crystal. Each substance possesses its own unique diffraction pattern because of the particular spatial electronic density distribution of atoms in the material. Various films were analyzed to determine if they were crystalline and, if so, what were their crystalline compositions. Samples were analyzed with a Phillips Electronics X-ray Diffractometer (Type 12045). This instrument is a full wave X-ray generator: stepless control, 10 to 60 KV and 2 to 50 MA, with a diffraction tube shield, X-ray port shutter and filter selector discs. A copper target, wide range goniometer (Type 4220-2) and an electronics circuit panel (Type 12096) completed the equipment configuration. Analyses were performed from 20-89°. Samples were obtained by scraping the films from the Pt foils onto which they had been electrodeposited.
X-ray Fluorescence (XRF) - When a sample is irradiated with a beam of X-rays, the X-rays are absorbed and produce electronically excited ions. These ions return to their ground state via a series of electronic transitions, emitting X-rays that are characteristic of the atoms comprising the particular sample. This method was used to determine the elemental composition of electrodeposited films. Films on Pt foils were analyzed with a Phillips Electronics X-ray Fluorescence Spectrometer (Type 12215). The unit is a constant potential X-ray generator: stepless control, 10 to 50 KV and 2 to 50 MA, with X-ray port shutters, filter selector discs and rectifier valves. Also included in the system are a wide range goniometer, tungsten target and a Hewlett-Packard (Model 7127A) strip chart recorder. A Canberra linear ratemeter (Model 1480), high-voltage power supply, amplifier and analyzer completed the make-up of the spectrometer system. Since this method was used for qualitative analyses, the X-ray tube was operated at the highest permissible voltage for best results. Scans were performed from 25-40° to determine if Ga and/or As were present. If Ga and As were present, peaks, corresponding to fluorescence lines, were observed at the following 20
angles (LiF): 30.5° and 34.0°, confirming the presence of As, and 35.0° and 38.9°, confirming the presence of Ga. Since the films were usually analyzed on Pt foils (2θ angles (LiF) at 32.3° and 38.1°), special experimental care was required to ascertain the presence of the Ga peak at 38.9°.
3.1 INTRODUCTION

Gallium is presently produced electrochemically as a by-product of the Al industry. Unfortunate is the best word to describe the lack of applications and importance of the element, which possesses the greatest liquid range. In 1965, the price of Ga was similar to the then price of Au ($1.1 per g) and though the price of Ga has slowly declined it remains a relatively expensive material. Today, its major use is in semiconductor technology but even this application only accounts for a small amount of the Ga supply produced by the Al industry each year. The emergence of GaAs solar cells, which possess high conversion efficiencies, is producing an additional market for Ga consumption. However, analysis of GaAs for large-scale power generation concludes that Ga is a very expensive material and that supplies are severely limited. Furthermore, some critics state that prospects for large scale use of GaAs solar cells are limited because production of large amounts of Ga, well above present production rates or reasonably foreseeable future production rates, would be required. It is ironic that Ga is involved in a perplexing cycle of cost
versus utility based on production of minimal amounts of available supplies.

Though the electrochemistry of Ga has received much attention in aqueous media, relatively little is known concerning the electrochemical kinetics of Ga species reduction in nonaqueous media. Verdieck and Yntema reported that solutions of Ga(III) in a AlCl₃-NaCl-KCl molten eutectic at 156°C showed a reduction process at + 0.83 V and deposition at about + 0.2 V vs. an Al metal reference electrode. Anders and Plambeck have investigated the electrochemistry of Ga in an AlCl₃-NaCl-KCl melt at 135°C. Using potentiometric and voltammetric techniques, they demonstrated that chloroaluminate melts favored the existence of the lower valence ionic species, i.e. Ga(I), more than water or chloride melts. Shafir and Plambeck reported that the stable oxidation states of gallium in a LiCl-KCl eutectic at 450°C are the metal and the trivalent ion. Tremillon and coworkers investigated the acidobasic properties of molten potassium tetrahalogenogallates. They reported that molten tetrahalogenogallates were chemically similar to tetrahalogenoaluminates, however, the existence of the
Ga(III) lower oxidation state complicated the determination of melt acidity. Recently, von Barner has reported the results of potentiometric investigations of the complex formation of Ga(III) in KCl-AlCl₃ melts at 300°C.

3.2 GALLIUM SPECIES VOLTAMMETRY

Our initial work involved studying the electrochemistry of Ga complexes in the low temperature AlCl₃:BPC melt using cyclic voltammetry, to better understand their redox properties. In many respects, the gallium chlorocomplexes exhibit behavior similar to aluminum chlorocomplexes. It is reasonable to postulate that the major species present in the acidic regime, i.e., 1:1 to 2:1 molar ratio AlCl₃:BPC respectively, include a mixed GaAlCl₇⁻ complex,

\[ \text{GaCl}_3 + \text{AlCl}_4^- \rightleftharpoons \text{GaAlCl}_7^- \quad (11) \]

and a Ga₂Cl₇⁻ complex,

\[ 2\text{GaCl}_3 + \text{Cl}^- \rightleftharpoons \text{Ga}_2\text{Cl}_7^- \quad (12) \]
However, in basic melts (molar ratio < 1:1), a tetra-chlorogallate species would be the corresponding major gallium species present,

\[ \text{GaCl}_3 + \text{Cl}^- \rightarrow \text{GaCl}_4^- \]  

(13)

Cyclic voltammetric investigations of Ga(III), added as GaCl₃ to acidic melts, showed two poorly defined reduction waves at approximately +0.87 V and +0.25 V vs. Al (2:1) reference. These are illustrated in Figure 3 for a 1.4:1 AlCl₃:BPC melt composition. The first reduction peak can be assigned the reduction of Ga(III) species to Ga(I) or Ga(0), and the second peak corresponds to the reduction of Ga(I) to Ga(0). Diagnostically, the first reduction peak, which is isolated in Figure 4, can be best described as a quasi-reversible reduction of Ga(III) to Ga(I) or Ga(0). For the reaction,

\[ \text{Ox} + n\text{e}^- \rightarrow \text{Red} \]  

(14)

certain diagnostic criteria are employed to best clarify the type of charge transfer which occurs. In the case of the reduction of Ga(III), the following criteria were used to determine that a quasi-reversible process was involved:
CV of approximately 48 mM Ga(III) at 200 mV/s, Pt button area 0.810 mm$^2$, in 1.4:1 AlCl$_3$:BPC, 30°C.
CV of approximately 16 mM Ga(III) at 50, 100 and 200 mV/s, Pt button area 0.810 mm$^2$, in 1.37:1 AlCl$_3$:BPC, 30°C.
1) $E_p$ (peak potential) shifts with $\nu$ (scan rate),
2) $E_p^c - E_p^a$ may approach 60/n mV at low $\nu$ but increases as $\nu$ increases, and
3) $i_p$ (peak current)/$\nu^{1/2}$ is virtually independent of $\nu$.\(^1\)

Table III contains $E_p$ and $i_p$ data as a function of scan rate for typical cyclic voltammograms of Ga(III) in the low temperature chloroaluminate melts. Unfortunately, in low temperature chloroaluminate melts the Ga(III) reduction reaction does not give well defined peaks on the forward (negative going) sweep and it is feasible that the reaction is complicated by the involvement of some other mixed oxidation state, perhaps a Ga(II) species or a complete reduction to Ga(0).

For a 2$e^-$ reduction followed by a 1$e^-$ reduction, it is expected that the reduction currents of the first peak will be approximately twice as large as those of the second peak. At intermediate melt acidities (e.g., 1.1:1 to 1.6:1) the first reduction peak was smaller than that of the second. However, as the melt acidity was increased by AlCl$_3$ addition to (2:1), the first peak became more regular in form and its currents became
<table>
<thead>
<tr>
<th>Molar Composition</th>
<th>Scan Rate (mV/s)</th>
<th>E_p (V)</th>
<th>i_p (μA)</th>
<th>E'_p (V)</th>
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<tr>
<td>1.6:1^b</td>
<td>500</td>
<td>0.87</td>
<td>22</td>
<td>0.24</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.90</td>
<td>10</td>
<td>0.30</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0.91</td>
<td>6</td>
<td>0.33</td>
<td>8</td>
</tr>
</tbody>
</table>

a) ~48 mM Ga(III), Pt Working Electrode, 35°C
b) ~38 mM Ga(III), Pt Working Electrode, 30°C
larger than those of the second peak (Figure 5), especially at faster scan rates. Therefore, with high melt acidity and fast scan rates, the reduction currents exhibited behavior more consistent with the ideal two-step mechanism,

\[
\text{Ga(III)} + 2e^- \rightarrow \text{Ga(I)} \quad (15)
\]

\[
\text{Ga(I)} + e^- \rightarrow \text{Ga(0)} \quad (16)
\]

In the presence of an excess of Ga(III), the following equilibrium would explain spontaneous loss of any gallium metal film and might account for the larger second reduction wave at low melt acidities,

\[
\text{Ga(III)} + 2\text{Ga(0)} \rightleftharpoons 3\text{Ga(I)} \quad (17)
\]

Cyclic voltammetric studies also were performed using AlCl\textsubscript{3}:MEIC melts at various melt compositions. The Ga(III), added as GaCl\textsubscript{3} to the AlCl\textsubscript{3}:MEIC melts, exhibited behavior similar to that obtained when added to AlCl\textsubscript{3}:BPC melts. Two poorly defined reduction waves, Ga(III)/Ga(I) (or Ga(0)) reduction followed by Ga(I)/Ga(0) reduction, occur in the acidic regime. However, an oxidation peak in the acidic AlCl\textsubscript{3}:MEIC
FIGURE 5

CV of approximately 44 mM Ga(III) at 500 mV/s,
Pt button area 0.810 mm², in 1.8:1 AlCl₃:BPC, 30°C.
melts, at approximately +1.3 V vs. Al (1.5:1) reference (Figure 6) is sharper than the oxidation peak in the corresponding AlCl\textsubscript{3}\textsuperscript{BPC} melts. The sharp anodic peak at circa +1.3 V presumably is the Ga(0) stripping peak and the shoulder at positive potentials may be due to Ga(I)/Ga(III) oxidation. Especially at scan rates below 100 mV/s, stripping peaks were obtained which possessed shoulders. Broad stripping peaks or stripping peaks with shoulders are likely to be indicative of composite behavior of two or more species being oxidized.

It has been reported previously that Ga(III) species in a KCl melt at 300°C could not be reduced directly to Ga(0).\textsuperscript{69} Although gallium chlorocomplexes behave in many respects similar to aluminum chlorocomplexes, unlike the Ga(I) ion, the Al(I) species has not been shown to be prevalent in either acidic or basic chloroaluminate melt media at 175°C.\textsuperscript{72} In low temperature basic chloroaluminate melts, it was not possible to reduce the GaCl\textsubscript{4}\textsuperscript{−} species prior to reduction of the butylpyridinium cation. Thus, attempts to electrodeposit gallium in basic melts were unproductive. Cyclic voltammetric studies did not produce good current responses of Ga(I) species (produced
CV of approximately 30 mM Ga(III) at 50 mV/s, with electrode area 7.06 mm², in 1:1:1 AlCl₃:MEIC, 25°C.
by constant potential electrolysis and added to the melt) in the basic regime.

In these electrochemical studies of Ga(III) in low temperature chloroaluminate melts, glassy carbon, tungsten and platinum working electrodes were employed for cyclic voltammetry. However, the best electrochemical responses were achieved at platinum.

3.3 POTENTIOMETRIC INVESTIGATIONS

In order to better understand the Ga redox properties and complex species in low temperature melts, constant potential electrolysis was performed on chloroaluminate melts containing Ga(III) ions to study the formation and stability of Ga(I) ion species. An exhaustive two-electron reduction theoretically would deplete the melt entirely of Ga(III) species, allowing electrochemical and physical examination of the Ga(I) ion species. Figure 7 contains a cyclic voltammogram of a 1.37:1 AlCl₃:BPC melt after partial reduction of the Ga(III) to Ga(I). The reduction of Ga(I) occurs as a single reduction peak at circa +0.25 V vs. Al (2:1) reference. Not only does the cathodic peak for Ga(I)
FIGURE 7

CV of approximately 16 mM Ga(III) at 50 mV/s after partial electrolysis, Pt button area 0.810 mm², in 1.37:1 AlCl₃:BPC, 30°C.
reduction show better structure, but the stripping peak is now better resolved because of the reduced Ga(III) activity. This effect can be clearly seen with the Ga(I) oxidation peak presumably occurring as a separate peak at about +1.4 V vs. Al (2:1) reference.

Anodization studies to obtain data concerning the electrochemistry of Ga(I) in the chloroaluminate melts also were performed. To determine the standard reduction potential, \( E_o \), of the Ga(I)/Ga(0) couple, a Nernst plot was constructed. The Nernst plot shown in Figure 8 was obtained by varying the Ga(I) ion concentration (anodization of a Ga electrode at low current densities) in a 1.5:1 acidic AlCl\(_3\):BPC melt and measuring the emf of a Ga(0) electrode vs. an Al (2:1) reference electrode. For the Ga(I) ion mole fraction range \( 3.27 \times 10^{-4} \) to \( 2.04 \times 10^{-2} \), the least squares slope was calculated to be 59 ± 2 mV (theory value 2.303 RT/nF at 35°C is 61 mV) and the intercept value for the standard electrode potential on the mole fraction scale is \( E_o = 0.339 \pm 0.005 \) V vs. Al (2:1) reference.

Potentiometric titrations of AlCl\(_3\):BPC melts containing a fixed mole fraction of Ga(I) were performed by
FIGURE 8

Nernst plot of Ga(I) in 1.5:1 AlCl₃:BPC melt, 35°C.
addition of BPC. The potentiometric measurements involving the Ga(I)/Ga(0) couple were carried out by use of the cell formally depicted by

$$\text{Al}\mid (2:1) \text{AlCl}_3 : \text{BPC}\mid \text{fritted disk}\mid \text{AlCl}_3 : \text{BPC, Ga(I)}\mid \text{Ga}$$  \hspace{1cm} (18)

Emf measurements were made vs. an Al (2:1) reference electrode as a function of melt composition with a high impedance voltmeter. Typical data are illustrated in Figure 9. It may be noted that in the acidic composition range the Ga(I) ion potential is practically unaffected by the melt acidity. This may mean that Ga(I) is uncomplexed or in a complex form which does not vary with the melt acidity.

The formation of various types of mononuclear chloro complex ions of the type \( \text{GaCl}^{1-m}_m \) was considered in the basic \( \text{AlCl}_3 : \text{BPC} \) melt. Information concerning the identity and stability of these complex ions can be obtained by curve fitting basic melt titration data to the expression

$$E = E_0 + \frac{RT}{F} \ln X_{\text{GaCl}^{1-m}_m} + \frac{RT}{F} \ln K - \frac{mRT}{F} \ln X_{\text{Cl}^-} + E_j$$  \hspace{1cm} (19)
Potentiometric titration of Ga(I) in AlCl$_3$·BPC, 35°C.
where the equilibrium constant, $K$, is defined by

$$K = X_{\text{Ga(I)}} (X_{\text{Cl}^-})^m \frac{X_{\text{GaCl}_2}^{1-m}}{X_{\text{GaCl}_1}^{m}}$$

(Eq. 20)

$E_j$, the cell liquid junction potential, can be assumed small and neglected. The Ga(I) ion mole fraction in the basic composition range can be calculated at each of the measured emf values from the Nernst equation,

$$E = E_0 + \frac{RT}{F} \ln \tilde{a}_{\text{Ga(I)}}$$

(Eq. 21)

using the standard electrode potential and assuming the activity of Ga(I) approximates the mole fraction of Ga(I). Representative data associated with the ion mole fractions for the potentiometric titration of Ga(I) are contained in Tables IV and V. Analysis of the potentiometric titration data indicated that Ga(I) is complexed most likely as $\text{GaCl}_2^-$ in the basic melt. Table IV contains data obtained after the reduction of Ga(III) to Ga(I) in a 1.5:1 AlCl$_3$:BPC melt. The data contained in Table V was obtained after the anodization of a gallium electrode in a 1.25:1 AlCl$_3$:BPC melt to produce Ga(I).

Figure 10 contains a plot of $E$ vs. Log $X_{\text{Cl}^-}$ constructed from the data shown in Tables IV and V.
Table IV. Ion Mole Fractions and Potentials for Titration of $4.64 \times 10^{-3}$ M Ga(I) in a 1.5:1 AlCl$_3$:BPC Melt at 35°C.

<table>
<thead>
<tr>
<th>E, V</th>
<th>Ga(I)</th>
<th>Cl$^-$ in excess to 1:1</th>
<th>GaCl$_2^-$</th>
<th>Cl$^-$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.963</td>
<td>5.21 x 10$^{-22}$</td>
<td>1.63 x 10$^{-2}$</td>
<td>4.39 x 10$^{-4}$</td>
<td>1.55 x 10$^{-2}$</td>
</tr>
<tr>
<td>-0.968</td>
<td>4.28 x 10$^{-22}$</td>
<td>3.99 x 10$^{-2}$</td>
<td>4.28 x 10$^{-4}$</td>
<td>3.90 x 10$^{-2}$</td>
</tr>
<tr>
<td>-1.026</td>
<td>4.76 x 10$^{-23}$</td>
<td>7.23 x 10$^{-2}$</td>
<td>4.14 x 10$^{-4}$</td>
<td>7.15 x 10$^{-2}$</td>
</tr>
<tr>
<td>-1.049</td>
<td>2.02 x 10$^{-23}$</td>
<td>1.11 x 10$^{-1}$</td>
<td>3.97 x 10$^{-4}$</td>
<td>1.11 x 10$^{-1}$</td>
</tr>
<tr>
<td>-1.065</td>
<td>1.12 x 10$^{-23}$</td>
<td>1.64 x 10$^{-1}$</td>
<td>3.73 x 10$^{-4}$</td>
<td>1.63 x 10$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$ Excess chloride ion fraction less the amount complexed with Ga(I)
Table V. Potentials and Ion Mole Fractions for Titration of 5.93 x 10^{-2} M Ga(I) in a 1.25:1 AlCl₃:BPC Melt at 40°C.

<table>
<thead>
<tr>
<th>E, V</th>
<th>Ga(I)</th>
<th>Cl⁻ in excess to 1:1</th>
<th>GaCl₂⁻</th>
<th>Cl⁻ a</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.920</td>
<td>2.57 x 10⁻²¹</td>
<td>1.02 x 10⁻²</td>
<td>6.01 x 10⁻³</td>
<td>6.16 x 10⁻³</td>
</tr>
<tr>
<td>-0.983</td>
<td>2.32 x 10⁻²²</td>
<td>2.94 x 10⁻²</td>
<td>5.94 x 10⁻³</td>
<td>1.75 x 10⁻²</td>
</tr>
<tr>
<td>-1.002</td>
<td>1.15 x 10⁻²²</td>
<td>4.53 x 10⁻²</td>
<td>5.88 x 10⁻³</td>
<td>3.33 x 10⁻²</td>
</tr>
<tr>
<td>-1.021</td>
<td>5.69 x 10⁻²³</td>
<td>6.54 x 10⁻²</td>
<td>5.72 x 10⁻³</td>
<td>5.39 x 10⁻²</td>
</tr>
<tr>
<td>-1.037</td>
<td>3.069 x 10⁻²³</td>
<td>8.90 x 10⁻²</td>
<td>5.58 x 10⁻³</td>
<td>7.78 x 10⁻²</td>
</tr>
<tr>
<td>-1.054</td>
<td>1.65 x 10⁻²³</td>
<td>1.06 x 10⁻¹</td>
<td>5.47 x 10⁻³</td>
<td>9.52 x 10⁻²</td>
</tr>
</tbody>
</table>

a) Excess chloride ion fraction less the amount complexed with Ga(I)
Variation of the cell potential with the calculated chloride ion mole fraction in basic AlCl$_3$:BPC

(▲) Basic emf values at 35°C, Ga(I) produced by reduction of Ga(III)
(●) Basic emf values at 40°C, Ga(I) produced by anodization of Ga(0) working electrode
(indicating a second-power dependence on chloride ion). For the basic emf values obtained from Table IV, a graph of emf vs. Log $X_{Cl^-}$ gave a line of slope $0.110 \pm 0.01$ V (theory value at 35°C is 0.122 V) with a correlation coefficient of 0.95. The least-squares slope of the data from Table V plotted in Figure 10 is $0.106 \pm 0.008$ V (theory value at 40°C is 0.124 V) with a correlation coefficient of 0.99. Deviation from ideality with respect to the second-power dependence on chloride ion mole fraction indicates the presence of adventitious oxidants. The presence of these oxidants caused difficulties in obtaining the expected emf values and may have resulted in a mixed potential being produced. However, it is reasonable to state that GaCl$_2^-$ is the predominant species in the basic regime.

3.4 ALUMINUM UNDERPOTENTIAL DEPOSITION

Deposition of a metal at potentials more positive than the thermodynamic reversible potential for the given conditions is a phenomenon termed underpotential deposition (UPD). This phenomenon precedes the bulk deposition of the metal which occurs negative to the reversible
potential. Metal ion adsorption occurs in an area described as the underpotential range, which may extend over a potential of a few hundred millivolts positive of the equilibrium potential. The underpotential, $E_u$, may be expressed by

$$E_u \approx E_0 + \frac{RT}{zF} \ln \frac{a_{M^{2+}}}{a_M}$$  \hspace{1cm} (22)

In this expression, $E_0$ is the equilibrium potential of the deposited metal-metal ion electrode.

The deposition of a metal at potentials significantly positive to that of bulk deposition has been observed in aqueous systems for Ag(I), Tl(I), and Cu(II) on Au.\textsuperscript{73} In addition, this same phenomenon is well known with regards to the formation of a monolayer of atomic hydrogen on Ir, Pt, and Rh electrodes.\textsuperscript{74} Using a LiCl-KCl molten salt system, Schmidt investigated the deposition of Ag(I), Cd(II), Ni(II) and Pb(II) ions and briefly addressed monolayer formation processes.\textsuperscript{75} Hills et al. studied the deposition of Ag and Ni on Pt from the LiCl-KCl eutectic at 400\textdegree C.\textsuperscript{76} They observed predeposition of Ni at 0.5 V positive to the equilibrium
potential, and predeposition of Ag at 0.1 V positive to the reversible potential.

During investigations of the electrochemistry of gallium in the room temperature chloroaluminate melts, cyclic voltammograms were obtained that perhaps indicated the presence of the UPD phenomenon. Figure 11 contains a voltammogram of Ga(III) at a slow scan rate (5 mV/s) in a very acidic, AlCl$_3$:BPC melt. After the second reduction wave, Ga(I) $\rightarrow$ Ga(0), a third, sharp reduction wave was obtained. This reduction peak at circa +0.16 V vs. Al (2:1) reference is presumably the underpotential deposition of Al onto Ga. After reversing the direction of the voltammetric sweep, an anodic peak (Al stripping) was obtained at approximately +0.24 V. Successive scans past 0.0 V showed that bulk deposition of Al occurred at potentials near -0.1 V vs. Al (2:1) reference. Thus, the underpotential deposition occurs at a potential about 0.15 V positive of the equilibrium potential. Integration of the currents, for the UPD of Al and the subsequent stripping, showed that the charge for Al predeposition on the cathodic sweep is nearly equal to the charge on the anodic sweep. The UPD phenomenon has been explained in
CV of approximately 15 mM Ga(III) at 5 mV/s.

Pt button area 0.810 mm$^2$, in 1.87:1 AlCl$_3$:BPC, 40°C.
terms of the existence of stronger attractive forces between atoms of the depositing metal and foreign atoms of a substrate than between similar atoms of the bulk metal. It is difficult to state if a GaAl intermetallic compound is responsible for this effect. This appears to be the first reported case for Al UPD.

3.5 FAST ATOM BOMBARDMENT (FAB) MASS SPECTROMETRY OF CHLOROALUMINATE MELTS

The technique of FAB mass spectrometry was pioneered by Barber and coworkers. They developed an ion source which accommodates solid materials (high molecular weight compounds of biological and biomedical importance), utilizes the phenomenon of ion sputtering and employs a beam of fast neutral atoms. This lower-energy particle bombardment technique does not require thermal sample volatilization and thus avoids direct thermal decomposition. In addition, the method works in either polarity while providing structurally significant fragmentation. Bojeson demonstrated that the application of this technique to inorganic salts was a natural extension. By his investigations of coordination compounds, Bojeson
showed that FAB mass spectrometry was a very useful analytical tool in the analysis of coordination compounds. Recently, Ackerman et al. have reported FAB mass spectrometric analyses (positive ion mode) of AlCl$_3$:BPC melts. Although characteristic changes in the positive ion FAB mass spectra reflected changes in melt composition, an overall assessment of the anions present was not possible from their data.

Recent investigations using lower-energy particle bombardment techniques have shown that the results obtained reflect the chemistry of condensed phase samples. Since the room temperature molten salts are ionic liquids, FAB mass spectrometric analysis seemed ideally suited for investigating the nature of the Al and Ga species present. Negative ion data, in particular, would provide a wealth of information concerning the metal complex ion species in room temperature melts, including those that comprise the melts themselves, as a function of changing Lewis acidity.
FAB Analysis of Acidic Chloroaluminate Melts

FAB mass spectra of two acidic chloroaluminate melts are shown in Figures 12 and 13. Figure 12 represents an averaged spectrum for the five intermediate analyses of a 2:1 mole ratio AlCl₃:BPC sample. Figure 13 shows an averaged spectrum for the five intermediate analyses of a 1.5:1 AlCl₃:MEIC sample. These samples were analyzed as negative ion spectra to determine the type of Al species present. In addition, analyses of two acidic melts with different organic components would allow a more facile assignment of resultant mass peaks. In principle, the presence of similar peaks would indicate common chloro, hydroxychloro or oxychloro species, while the presence of different peaks would indicate species arising from dissimilar organic BP⁺ and MEI⁺ fragments.

Observation of Figures 12 and 13 shows that the most intense peak in each spectrum occurs at m/z 169, corresponding to the tetrachloroaluminate species. Interestingly, the intensity of the heptachlorodialuminate species at m/z 301 is unexpectedly low. Apparently, Al₂Cl₇⁻ is highly susceptible to fragmentation and less stable in the FAB environment than in the liquid phase,
Figure 12

FAB mass spectrum of a 2:1 AlCl$_3$:BPC melt.
FIGURE 13

FAB mass spectrum of a 1.5:1 AlCl₃:MEIC melt.
where the main evidence for its presence is Raman spectroscopy. Table VI contains peak assignments and relative intensities for major clusters in the spectra. In all cases, the chlorine isotope distribution pattern obtained exactly matches the theoretical pattern and the resultant peak atomic mass units closely match the theoretical mass values.

Two important conclusions can be made from the information in Table VI. First, in addition to the chloroaluminate species, a variety of hydroxychloro and oxychloro species have been observed. Secondly, an important aspect of the condensed phase chemistry is reflected in the results, because the relative intensities of the oxychloro and hydroxychloro species differ in the BPC and MEIC melt spectra. Consistent with observations made in the laboratory from handling these melts, the lower affinity for oxygen and water of the MEIC based melts over the BPC based melts may be due, in part, to the greater hygroscopic character of BPC. Though the oxychloro and hydroxychloro species detected above m/z 320 may only be FAB gas phase reaction products, there exists evidence for their presence in the liquid and
Table VI. Summary of FAB Spectra of Acidic Chloro-
aluminate Melts.

<table>
<thead>
<tr>
<th>m/z</th>
<th>2:1 AlCl₃:BPC*</th>
<th>1.5:1 AlCl₃:MEIC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>149</td>
<td>AlCl₃OH⁻</td>
<td>AlCl₃OH⁻</td>
</tr>
<tr>
<td>169</td>
<td>AlCl₄⁻</td>
<td>AlCl₄⁻</td>
</tr>
<tr>
<td>247</td>
<td>Al₂OCl₅⁻</td>
<td>Al₂OCl₅⁻</td>
</tr>
<tr>
<td>283</td>
<td>Al₂Cl₆OH⁻</td>
<td>Al₂Cl₆OH⁻</td>
</tr>
<tr>
<td>301</td>
<td>Al₂Cl₇⁻</td>
<td>Al₂Cl₇⁻</td>
</tr>
<tr>
<td>325</td>
<td>Al₃Cl₆O₂⁻</td>
<td>Al₃Cl₆O₂⁻</td>
</tr>
<tr>
<td>361</td>
<td>Al₃Cl₇O₂H⁻</td>
<td>Al₃Cl₇O₂H⁻</td>
</tr>
<tr>
<td>381</td>
<td>Al₃Cl₈O⁻</td>
<td>Al₃Cl₈O⁻</td>
</tr>
<tr>
<td>399</td>
<td>Al₃Cl₉⁻</td>
<td>-----</td>
</tr>
<tr>
<td>459</td>
<td>Al₄Cl₉O₂⁻</td>
<td>Al₄Cl₉O₂⁻</td>
</tr>
</tbody>
</table>

*Relative intensities (%) in parenthesis
solid phases. Berg and coworkers have reported that structurally satisfactory molecular ions such as $\text{Al}_3\text{O}_2\text{Cl}_6^-$ are likely to exist in chloroaluminate melts. They postulated that $\text{AlOC}_1$ dimeric solvated species form to produce species such as $\text{Al}_3\text{O}_2\text{Cl}_6^-$ and $\text{Al}_4\text{O}_2\text{Cl}_{10}^{2-}$. Thewalt and Stollmaier have reported X-ray structure analyses characterizing products containing chlorooxoaluminate ions such as $\text{Al}_3\text{OCl}_8^-$ and $\text{Al}_4\text{O}_2\text{Cl}_{10}^{2-}$. Thus, FAB analyses have detected species confirmed by potentiometry and Raman analyses along with recently detected novel oxychloro anions.

**FAB Analysis of a Basic Chloroaluminate Melt**

Figure 14 contains a FAB mass spectrum of a basic $\text{AlCl}_3$:MEIC melt. Similar to the acidic chloroaluminate melts, the most intense peak is again at $m/z$ 169, corresponding to the tetrachloroaluminate species. The overall lack of hydroxychloro and oxychloro species in the basic melt may reflect the greater reactivity of melts containing an excess of aluminum chloride. Table VII contains a summary of the major clusters obtained for a typical FAB analysis of a basic chloroaluminate melt.
FIGURE 14

FAB mass spectrum of a 0.86:1 AlCl₃:MEIC melt.
Table VII. Summary of FAB Spectra in a Basic AlCl$_3$: MEIC Melt.

<table>
<thead>
<tr>
<th>m/z</th>
<th>0.86:1 AlCl$_3$:MEIC</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>158</td>
<td>AlCl$_3$C$_2$H$_2^-$</td>
<td>9</td>
</tr>
<tr>
<td>169</td>
<td>AlCl$_4^-$</td>
<td>100</td>
</tr>
<tr>
<td>247</td>
<td>Al$_2$OCl$_5^-$</td>
<td>8</td>
</tr>
<tr>
<td>301</td>
<td>Al$_2$Cl$_7^-$</td>
<td>16</td>
</tr>
<tr>
<td>449</td>
<td>[(AlCl$_4^-$)$_2$MEI$^+$]$^-</td>
<td>$</td>
</tr>
</tbody>
</table>
The two major clusters correspond to the tetrachloro and heptachloro species of Al. The most abundant oxide species occurs at m/z 247 and is reduced to only eight percent of the most intense peak. The cluster at m/z 449, corresponding to \[(\text{AlCl}_4^-)_2\text{MEI}^+\]−, is a clear example of ion pairing which occurs in the FAB environment. Previously, Ackerman et al. have reported observing a cluster corresponding to \[(\text{BP}^+)_2\text{AlCl}_4^-\] in a positive ion FAB mass spectrum.\(^{80}\) A calculated isotopic distribution pattern of the MEI\(^+\) based cluster is located on the inset of Figure 14. The larger peaks correspond to the chlorine isotopic pattern, while the smaller isotopic pattern illustrates the effect of the presence of carbon atoms in the molecule. This cluster, also may occur in the FAB spectra of the acidic MEIC based chloroaluminate melt, but it is somewhat obscured by the cluster at m/z 459. Once again, the results obtained experimentally are in good agreement with the calculated isotopic distribution patterns.
FAB Analysis of Chloroaluminate Melts Containing Ga(III)

With the identification of the various Al species obtained by FAB analysis of the chloroaluminate melts, the next objective was to investigate chloroaluminate melts containing added Ga(III). A one microliter sample of a 3.244 g 1.48:1 AlCl₃:BPc melt containing 0.279 g of GaCl₃ was analyzed and the resultant FAB mass spectrum is shown in Figure 15.

Overall, Figure 15 is similar to Figure 12 which contained the FAB mass spectrum of an acidic BPc based chloroaluminate melt without added Ga(III). One major difference is the decreased relative intensity of all oxychloro and hydroxychloro species. Quite possibly this effect can be due to the analysis of a freshly prepared acidic sample containing Ga(III) versus an old, slightly discolored acidic melt. This effect also may be due to the different atmospheric conditions present when the probe was transferred into the vacuum port. The melts were exposed to the atmosphere briefly (less than ten seconds) because the inlet port of the instrument was not equipped for anaerobic sampling. Another important difference is the cluster at m/z 211, corresponding to
FAB mass spectrum of a 1.48:1 AlCl$_3$:BPC melt containing GaCl$_3$. 
the tetrachlorogallate species. Somewhat unexpected is the fact that it is the second most intense peak in the spectrum. While other clusters of Ga complexes were expected and perhaps mixed Ga-Al complexes, none could be detected in these spectra. This effect possibly could be due to the low relative concentration of Ga to Al.

Table VIII contains a summary of the peak clusters for an acidic melt with Ga(III). It clearly demonstrates an important difference from earlier spectra, particularly from m/z 97 to m/z 169. Clusters at m/z 97, 132 and 169 corresponding to \( \text{AlCl}_2^- \), \( \text{AlCl}_3^- \) and \( \text{AlCl}_4^- \) clearly indicate chlorocomplexes for Al in three oxidation states, two of which are subvalent states. Subvalent Al species, which are known to exist in the gas phase, have been previously detected by mass spectrometry. Since the FAB environment involves collisional decomposition, the detection of the subvalent Al chlorocomplexes is interesting but not surprising. Of further interest is the cluster at m/z 132 which can be accounted for by assuming the presence of a monomer/dimer combination (\( \text{AlCl}_3^-/\text{Al}_2\text{Cl}_6^{2-} \)). The existence of aluminum(II) chloride and its dimer were first reported by Chai and
Table VIII. Summary of FAB Spectra of 1.48:1
AlCl₃: BPC Containing GaCl₃.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Assignment</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>AlCl₂⁻</td>
<td>10</td>
</tr>
<tr>
<td>132</td>
<td>AlCl₃⁻</td>
<td>15</td>
</tr>
<tr>
<td>158</td>
<td>AlCl₃C₂H₂⁻</td>
<td>50</td>
</tr>
<tr>
<td>169</td>
<td>AlCl₄⁻</td>
<td>100</td>
</tr>
<tr>
<td>211</td>
<td>GaCl₴⁻</td>
<td>74</td>
</tr>
<tr>
<td>247</td>
<td>Al₂OCl₅⁻</td>
<td>61</td>
</tr>
<tr>
<td>283</td>
<td>Al₂Cl₆OH⁻</td>
<td>55</td>
</tr>
<tr>
<td>301</td>
<td>Al₂Cl₇⁻</td>
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<tr>
<td>325</td>
<td>Al₃Cl₆O₂⁻</td>
<td>56</td>
</tr>
<tr>
<td>381</td>
<td>Al₃Cl₈O⁻</td>
<td>35</td>
</tr>
<tr>
<td>458</td>
<td>Al₄Cl₉O₂⁻</td>
<td>50</td>
</tr>
</tbody>
</table>
coworkers. Their gas phase studies were performed to obtain thermodynamic data for the previously unreported Al(II) species. While doubly charged ions are rare in desorption mass spectrometry, they are more easily observed in field desorption than in fast atom bombardment. It should be noted that the Al(II) peak is larger than the peak for Al(I), suggesting successive loss of Cl atoms by collision. In principle, the dimers may form by two collisions or by additive dimerization.

Next, a sample taken from a 1.698 g 0.82:1 AlCl₃:MEIC melt containing 0.042 g of GaCl₃ was analyzed by FAB mass spectrometry. Figure 16 contains a typical FAB mass spectrum obtained for this sample. Similar to the previously analyzed acidic melt, the two largest peaks occur at m/z 169 and 211, corresponding to the tetra-chloro- species of Al and Ga, respectively. Once again, the oxychloro and hydroxychloro peaks in the basic melt are much less intense than those in an acidic melt with Ga(III). It is interesting to note that when GaCl₃ is added to a basic and/or acidic chloroaluminate melt the peak intensity of the cluster at m/z 301, corresponding to Al₂Cl₇⁻, is significantly increased. Table IX
FAB mass spectrum of a 0.82:1 AlCl₃:MEIC melt containing GaCl₃.
Table IX. Summary of FAB Spectra of 0.82:1 AlCl₃:
MEIC Containing GaCl₃.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Assignment</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>AlCl₂⁻</td>
<td>5</td>
</tr>
<tr>
<td>132</td>
<td>AlCl₃⁻</td>
<td>12</td>
</tr>
<tr>
<td>158</td>
<td>AlCl₃C₂H₂⁻</td>
<td>31</td>
</tr>
<tr>
<td>169</td>
<td>AlCl₄⁻</td>
<td>100</td>
</tr>
<tr>
<td>211</td>
<td>GaCl₄⁻</td>
<td>60</td>
</tr>
<tr>
<td>247</td>
<td>Al₂OCl₅⁻</td>
<td>50</td>
</tr>
<tr>
<td>283</td>
<td>Al₂Cl₆OH⁻</td>
<td>12</td>
</tr>
<tr>
<td>301</td>
<td>Al₂Cl₇⁻</td>
<td>49</td>
</tr>
<tr>
<td>449</td>
<td>[(AlCl₄⁻)₂MEI⁺]⁻</td>
<td>25</td>
</tr>
</tbody>
</table>
summarizes the FAB spectra obtained from the analysis of basic MEIC melts containing Ga(III). The Al subvalent chloro species were once again detected but with lower relative peak intensities than for acidic melts. It should be noted that the subvalent Al chlorocomplexes also appear in the melts with Ga(III), but at one-half to one-fifth the relative intensities found for acidic melts.

It is well known that oxygenation of chlorides from moisture or vessel corrosion are difficult to avoid in tetrachloroaluminate melts. In addition to oxygen, oxides and water, proton sources such as HCl may contribute to the formation of hydroxy and oxyhydroxy species. The determination of oxides in chloroaluminate melts has received much attention, since potentially they play an important role in the chemistry of the melts. Since the impurities which contribute to the oxidation of chlorides are always present in the melts, understanding their chemistry is quite important. FAB analyses have provided new evidence concerning the reaction products present in chloroaluminate melts. Of particular interest is the detection of greater amounts of oxychloro and
hydroxychloro species in acidic versus basic melts. Electrophilic attack of AlCl\textsubscript{3} on hydroxy groups (leading to HCl loss) could possibly explain the presence of larger amounts of oxide and hydroxy species in acidic melts. Basic melts contain much less free aluminum chloride than acidic melts and the above reaction would be expected to occur to a lesser extent in basic melts. Though much work still needs to be performed to understand fully the effect of oxides on melt chemistry, FAB analyses have provided some helpful insights and species identification.
4.1 INTRODUCTION

Though the primary objective of this research was to investigate the prospects of GaAs film formation from chloroaluminate melts, a secondary objective involved finding media suitable for possible thin film fabrication of III-V semiconductors. With respect to GaAs and GaP, a melt based on GaCl₃ would be an ideal prospect. Several low melting mixtures of GaCl₃ with metal chlorides are known to form. Some examples of halide based melts include: GaCl₃:ZnCl₂ (M.P. 30°C), GaCl₃:LiCl (M.P. 57°C) and GaCl₃:NaCl (M.P. 62°C). These melting points are relatively low but they represent the melting points for the respective eutectic mixtures. Since concurrent studies involved room temperature molten salts, we set out to find a gallium melt system with a reasonable liquidus range at or near room temperature.

As the organic halides (BPC and MEIC) were being used in low temperature chloroaluminate melts, they seemed likely candidates to form low temperature melts with GaCl₃. Preliminary studies showed that some mixtures of the solids GaCl₃ and BPC became liquid at or
near room temperature. In addition, since BPC based chlorogallate melts exist, it seemed probable that MEIC based chlorogallate melts also might occur. Such media would eliminate any Al codeposition in GaAs film fabrication. However, before a critical evaluation of any new system can be made with regards to electrodeposition of materials, preliminary physical characterizations are helpful. With respect to the chlorogallate melts, melting points and general working parameters (i.e. thermal stability) needed to be established. Also, characterization of the electrochemical potential windows along with melt acid-base properties are necessary.

4.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC) OF CHLOROGALLATE MELTS

Various mixtures of GaCl$_3$ and BPC or MEIC have been found to be liquids at room temperature. When GaCl$_3$ is mixed with BPC or MEIC an exothermic reaction occurs. Slow gradual addition of GaCl$_3$ to either BPC or MEIC is required to control the exothermic reaction which results and to avoid melt decomposition. GaCl$_3$:BPC or GaCl$_3$:MEIC melts when properly prepared are clear, colorless liquids. The compositions of these melts may be expressed
as the mole fraction, N, of GaCl$_3$. Differential scanning calorimetry studies were performed on several samples from the two chlorogallate melt systems and the results are presented in the following section. Each sample was analyzed at least twice (usually at different scan rates) to determine transition temperatures and overall thermal stability. All samples exhibited good thermal stability to 125°C without any signs of decomposition.

**DSC Studies of BPC Based Melts**

Chlorogallate melts based on BPC were investigated in the 0.3 to 0.68 mole fraction composition range. The temperature range for each scan was -65°C to 125°C. Samples usually were cooled at -65°C for ten to twenty minutes before analysis. Table X contains a summary of DSC data for the acidic chlorogallate melts. For these melts, the melting points decrease with increasing acidity and then rise slightly. Though no samples of mole fraction greater than 0.68 were analyzed by DSC, visual examination of such melts showed an abrupt rise in transition temperatures. In fact, the transition temperatures for very acidic melts quickly rose to over 40°C. Thus, the liquidus range for acidic melts at 40°C
Table X. Summary of DSC Data for Acidic GaCl₃:BPC Melts.

| Mole Fraction | M.P. (°C) | ΔH (J/g) | Comments  
|---------------|-----------|----------|-----------
| 0.50         | 47.4      | 53.24    | 5°C/min   |
| 0.51         | 45.6      | 40.98    | 5°C/min   |
| 0.54         | 38.6      | 34.96    | 5°C/min   |
| 0.57         | 31.3      | 27.10    | 10°C/min  |
| 0.59         | -1.6      | 23.93    | CR, 5°C/min |
| 0.62         | 12.0      | 8.82     | CR, 5°C/min |
| 0.65 Unknown | -----     | Inconclusive |
| 0.68         | 6         | Possible Tg |

a) Crystalline rearrangement (CR) or glass transition (Tg) occurs where indicated.
appears to extend from $N=0.53$ to $N=0.7$. Figure 17 depicts a typical DSC scan of a neutral GaCl$_3$:BPC melt. Of particular interest, the neutral melt exhibits the highest melting point of the range of these mixtures analyzed by DSC and yielded typical endothermic behavior for a melting point. Additionally, it is noted that a trend of decreasing enthalpies of fusion exists with increasing melt acidity. Though only one sample was analyzed between mole fractions 0.62 and 0.68, it is quite probable that the transition temperatures are well below room temperature and involve glass transitions.

Table XI contains a summary of DSC data for basic GaCl$_3$:BPC melts. With increasing basicity, the melting points decrease gradually. At 35°C, the liquidus range of this molten salt system extends from mole fraction 0.47 to 0.29. Visual observation of melts of composition less than $N=0.30$ revealed that an abrupt increase occurs in transition temperatures. Of particular interest is the tendency of the basic melts to undergo crystalline rearrangements. Figure 18 contains a DSC scan for a basic melt which exhibited two crystalline rearrangements at -8°C and -30°C. This phenomenon is of interest because corresponding chloroaluminate systems do not show
DSC analysis of 30 mg GaCl$_3$:BPC (N=0.50) at 5°C/min.
<table>
<thead>
<tr>
<th>Mole Fraction</th>
<th>M.P. (°C)</th>
<th>ΔH (J/g)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.49</td>
<td>46.4</td>
<td>47.53</td>
<td>5°C/min</td>
</tr>
<tr>
<td>0.46</td>
<td>33.7</td>
<td>62.85</td>
<td>10°C/min</td>
</tr>
<tr>
<td>0.43</td>
<td>32.2</td>
<td>67.12</td>
<td>DCR, 5°C/min</td>
</tr>
<tr>
<td>0.40</td>
<td>30.6</td>
<td>64.59</td>
<td>DCR, 5°C/min</td>
</tr>
<tr>
<td>0.37</td>
<td>31.6</td>
<td>57.08</td>
<td>DCR, 5°C/min</td>
</tr>
<tr>
<td>0.34</td>
<td>31.5</td>
<td>52.45</td>
<td>CR, 5°C/min</td>
</tr>
<tr>
<td>0.30</td>
<td>30.7</td>
<td>45.96</td>
<td>5°C/min</td>
</tr>
</tbody>
</table>

a) crystalline rearrangement (CR), double crystalline rearrangement (DCR)
DSC analysis of 41 mg GaCl$_3$:BPC (N=0.40) at 5°C/min.
this behavior. These rearrangements exhibit typical exothermic behavior and, in general, had a greater tendency to be present in basic than acidic chlorogallate melts (BPC and MEIC).

**DSC Studies of MEIC Based Melts**

As anticipated, similar to BPC, MEIC when mixed with GaCl$_3$ also formed a molten salt. Several mixtures of GaCl$_3$ and MEIC, which formed liquids at room temperature, demonstrated that a new chlorogallate molten salt system existed. Chlorogallate melts based on MEIC were investigated in the mole fraction composition range of 0.28 to 0.84. Once again, the temperature range for each scan was -65°C to 125°C.

Table XII contains a summary of DSC data for the MEIC acidic melts. All chlorogallate melts in this system from the neutral melt to N=0.81 are liquid below room temperature. Comparison of the data in Tables X and XII reveals that the MEIC based acidic chlorogallate melts possess significantly lower transition temperatures (melting points or glass transitions) than corresponding BPC chlorogallate melts. This behavior is consistent
Table XII. Summary of DSC Data for Acidic GaCl₃:MEIC Melts.

<table>
<thead>
<tr>
<th>Mole Fraction</th>
<th>M.P. a (°C)</th>
<th>ΔH b (J/g)</th>
<th>Comments c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51</td>
<td>14.5</td>
<td>37.3</td>
<td>7°C/min</td>
</tr>
<tr>
<td>0.53</td>
<td>9.4</td>
<td>22.7</td>
<td>5°C/min</td>
</tr>
<tr>
<td>0.56</td>
<td>1.0</td>
<td>11.6</td>
<td>2°C/min</td>
</tr>
<tr>
<td>0.58</td>
<td>-3.2</td>
<td>12.4</td>
<td>5°C/min</td>
</tr>
<tr>
<td>0.60</td>
<td>-15.8</td>
<td>-0.87</td>
<td>Tg, 5°C/min</td>
</tr>
<tr>
<td>0.63, 0.66, 0.69, 0.71, 0.72, 0.73</td>
<td>Unknown Tg's (below -25)</td>
<td>-----</td>
<td>Inconclusive results</td>
</tr>
<tr>
<td>0.79</td>
<td>10.6</td>
<td>-----</td>
<td>Tg, 5°C/min</td>
</tr>
<tr>
<td>0.81</td>
<td>20.8</td>
<td>-0.31</td>
<td>Tg, 7°C/min</td>
</tr>
<tr>
<td>0.84</td>
<td>49.2</td>
<td>-0.24</td>
<td>Tg, 5°C/min</td>
</tr>
</tbody>
</table>

a) Glass transition temperatures provided when indicated.

b) For glass transitions - ΔCp (J/g°C) provided.

c) Glass transition (Tg) occurs.
with transition temperatures exhibited by MEIC based chloroaluminate melts versus BPC based chloroaluminate melts. Another interesting result is that all melts of GaCl₃ mole fraction greater than N=0.59 exhibited glass transitions. Figure 19 illustrates a DSC analysis of a N=0.60 melt. The glass transition at -15.8°C is a typical example of the endothermic behavior exhibited in the transitions of the higher acidity melts. Inconclusive results were obtained on analyses of melts between mole fractions N=0.62-0.74. Most likely these melts exhibit glass transitions but these could not be detected owing to experimental constraints. These experimental constraints include not being able to cool the samples to below -65°C and/or insufficient cooling periods which precluded the liquids from glassing or freezing.

Of further interest, the acidic liquidus range at room temperature is significantly greater for this chlorogallate molten salt system than for the MEIC chloroaluminate system. The melting point for a chloroaluminate melt (MEIC) at N=0.70 is 79°C, while the corresponding chlorogallate melt is a liquid below room temperature and even with further GaCl₃ addition remains a liquid until N=0.80. This greater acidic liquidus
FIGURE 19

DSC analysis of 18 mg GaCl$_3$:MEIC (N=0.60) at 5°C/min.
range, quite possibly, may allow the determination of gallium chlorocomplexes previously undetected in the liquid phase.

A summary of DSC date for basic GaCl$_3$:MEIC melts is contained in Table XIII. Once again, the MEIC based chlorogallate melts in the basic regime possess significantly lower melting points than their BPC counterparts. Approximately one-half of the basic samples experienced some type of crystalline rearrangement. From the neutral regime to $N=0.30$ the melts remained liquid at room temperature. With the exception of the most basic limits of the liquidus range, the highest melting point occurs for a neutral melt. Figure 20 contains a DSC analysis of a neutral melt. A sharp peak, indicating a melting point at 15.3°C, demonstrates typical endothermic behavior for the neutral melt. As the melt basicity is increased from the neutral regime, the melting points gradually decreased until approximately mole fraction $N=0.34$. The region from $N=0.36$ to $N=0.32$ quite possibly involves glass transitions. Unfortunately, these transitions could not be detected because of experimental difficulties in attaining the low temperatures required. At mole fractions lower than $N=0.32$, the melting points begin to
Table XIII. Summary of DSC Data for Basic GaCl₃:MEIC Melts.

<table>
<thead>
<tr>
<th>Mole Fraction</th>
<th>M.P. (°C)</th>
<th>ΔH (J/g)</th>
<th>Comments²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>15.3</td>
<td>40.94</td>
<td>5°C/min</td>
</tr>
<tr>
<td>0.47</td>
<td>10.5</td>
<td>25.59</td>
<td>5°C/min</td>
</tr>
<tr>
<td>0.45</td>
<td>7.0</td>
<td>14.91</td>
<td>5°C/min</td>
</tr>
<tr>
<td>0.44</td>
<td>3.5</td>
<td>41.31</td>
<td>CR, 5°C/min</td>
</tr>
<tr>
<td>0.42</td>
<td>3.1</td>
<td>40.08</td>
<td>CR, 5°C/min</td>
</tr>
<tr>
<td>0.41</td>
<td>1.0</td>
<td>40.74</td>
<td>CR, 4°C/min</td>
</tr>
<tr>
<td>0.39</td>
<td>5.5</td>
<td>39.44</td>
<td>CR, 5°C/min</td>
</tr>
<tr>
<td>0.36</td>
<td>0.6</td>
<td>1.46</td>
<td>10°C/min</td>
</tr>
<tr>
<td>0.34</td>
<td>Unknown</td>
<td>-----</td>
<td>Inconclusive</td>
</tr>
<tr>
<td>0.32</td>
<td>14.7</td>
<td>3.11</td>
<td>4°C/min</td>
</tr>
<tr>
<td>0.28</td>
<td>39.1</td>
<td>20.66</td>
<td>CR, 5°C/min</td>
</tr>
</tbody>
</table>

a) Crystalline rearrangement (CR) occurs prior to M.P.
DSC analysis of 20 mg GaCl$_3$·MEIC (N=0.50) at 5°C/min.
increase sharply with increase of basicity and the melts are no longer liquids at room temperature.

To develop a better overall view of the phase transitions involved in the chloroaluminate versus chlorogallate system, selected phase transition data for the MEIC based systems have been plotted in Figure 21. The available phase transition data are plotted for mole fractions N=0.28-0.84 and N=0.25-0.73 for the GaCl₃:MEIC and AlCl₃:MEIC systems, respectively. Qualitatively, the solid-liquid phase diagrams are similar. In addition, these phase diagrams are similar to that reported for AlCl₃:1-ethylpyridinium bromide binaries. Examination of the phase transition data for these room temperature molten salts reveals that these systems exhibit eutectic points near the N=0.33 and N=0.66 mole fraction compositions. In addition, within the N=0.33 and N=0.66 composition range there exists an apex of the liquid-solid phase diagrams at N=0.50, the neutral melt composition. Presumably, the apex at N=0.50 is due to the symmetry of the binary systems at neutral compositions. It should also be noted that the apex and the eutectic points correspond to changes in the major anionic species present in these melts. Quite clearly, these changes
Phase transition data for AlCl₃:MEIC⁹¹ and GaCl₃:MEIC.

AlCl₃:MEIC - (●) MP, (○) Tg
GaCl₃:MEIC - (■) MP, (□) Tg
coincide with qualitative pattern shifts in the phase
diagram of the room temperature melts. The lower temper­
atures for the acidic GaCl₃ melts over those for AlCl₃
based melts may reflect the lower melting point of the
former (Ga₂Cl₆ M.P.=77.9°C, Al₂Cl₆ M.P.=190°C at 2.5
atm).

4.3 ELECTROCHEMICAL WINDOWS FOR CHLOROGALLATE MELTS

Once the DSC studies had been completed and the
thermal behavior of the melts determined, the character­
ization of the electrochemical windows was performed to
determine their positive and negative limits. The
electrochemical windows were obtained by cyclic voltam­
metry for acidic, neutral and basic chlorogallate melts.
It should be noted that the voltammetric curves were
obtained on a W working electrode which, in general, is
more inert than Pt.

Figure 22 shows the electrochemical windows for
GaCl₃:BPC melts, while Figure 23 illustrates the electro­
chemical windows for GaCl₃:MEIC melts. The reference
electrode used for the BPC based chlorogallate melt
system voltammetry consisted of an Al wire immersed in a
Cyclic voltammetric curves of GaCl₃:BPC melts at 100 mV/s, W electrode area 7.06 mm², 40°C.
(a) Acidic GaCl₃:BPC (N=0.51)
(b) Neutral GaCl₃:BPC (N=0.50)
(c) Basic GaCl₃:BPC (N=0.48)
Cyclic voltammetric curves of GaCl$_3$:MEIC melts at 100 mV/s, W electrode area 7.06 mm$^2$, 30°C.
(a) Acidic GaCl$_3$:MEIC (N=0.53)
(b) Neutral GaCl$_3$:MEIC (N=0.50)
(c) Basic GaCl$_3$:MEIC (N=0.47)
N\textsubscript{0.60} AlCl\textsubscript{3}:BPC melt. An Al wire immersed in a N\textsubscript{0.60} AlCl\textsubscript{3}:MEIC melt served as the reference electrode for the GaCl\textsubscript{3}:MEIC system voltammetry. For acidic melts, N>0.50, the positive and negative limits are similar for both the GaCl\textsubscript{3}:BPC melt and the GaCl\textsubscript{3}:MEIC melt. It is reasonable that the positive limits correspond to chlorine evolution while the negative limits correspond to gallium deposition. In the basic regime, N<0.50, the positive limit again appears to correspond to the electrooxidation of chloride ions for both GaCl\textsubscript{3}:BPC and GaCl\textsubscript{3}:MEIC melts. The electroreduction of the organic cation, BP\textsuperscript{+} or MEI\textsuperscript{+}, appears to correspond to the negative limit of each respective melt. This was established by scanning into background and observing the products obtained on successive scans.

Similar to neutral AlCl\textsubscript{3}:RCl melts (R=BP\textsuperscript{+} or MEI\textsuperscript{+}), neutral GaCl\textsubscript{3}:RCl melts exhibit wide electrochemical windows.\textsuperscript{92} For a neutral GaCl\textsubscript{3}:BPC melt the electrochemical window is approximately 3.7 V. The electrochemical window is larger for a neutral GaCl\textsubscript{3}:MEIC melt and extends approximately 4.0 V. These melts offer unique possibilities for electrochemical investigations,
but even small changes in the acidity will greatly affect the electrochemical window. This statement is vividly demonstrated when one examines Figure 22, which contains the electrochemical windows of melts with gallium mole fractions equal to 0.48, 0.50 and 0.51.

4.4 RAMAN SPECTROSCOPY OF CHLOROGALLATE MELTS

Raman spectra of low temperature GaCl$_3$:MEIC molten salts have been obtained. The objective of the Raman spectroscopic investigation was to study the gallium species composition in the molten chlorogallate system for the $N=0.35$ to $N=0.77$ composition range. The MEIC chlorogallate system was selected, instead of the BPC chlorogallate system, because of its wider liquidus range at room temperature. Several gallium complexes may be postulated to exist in these melts, including GaCl$_4^-$, Ga$_2$Cl$_7^-$ and molecular gallium chloride. In addition, it was hoped that analysis of a $N=0.77$ melt might provide evidence for the Ga$_3$Cl$_{10}^-$ ion in the liquid phase. Once the $N=0.67$ melt composition is exceeded, the following reaction may be postulated to occur

$$2\text{Ga}_2\text{Cl}_7^- + \text{Ga}_2\text{Cl}_6 \rightarrow 2\text{Ga}_3\text{Cl}_{10}^-$$ (23)
Evidence has yet to be confirmed for the corresponding chloroaluminate melt ion, $\text{Al}_3\text{Cl}_{10}^-$. Thus, Raman studies of these melts were performed to characterize further the melts and to determine the major chlorogallate species present. Spectra were obtained with horizontal and vertical polarizations.

Figure 24 represents Raman spectra for $N=0.35$, (a), and $N=0.64$, (b), chlorogallate melts. Observation of spectra (a) and (b) show that the Raman frequency shifts are different, indicating the presence of different chlorogallate species in the basic versus acidic chlorogallate melts. Table XIV contains the Raman vibrational frequencies, together with information concerning intensity and polarization. Examination of the data summarized in Table XIV indicates that the major chlorogallate species, identical in the $N=0.35-0.50$ composition range, changes as the mole fraction progresses into the acidic region. In Figure 24, the upper spectrum in (a) and (b) was obtained with the exciting laser light polarized in the vertical plane, while the lower spectrum in (a) and (b) was obtained with horizontal polarization. As is evidenced in this figure, the totally symmetric
Raman spectra of GaCl$_3$:MEIC melts where (a) and (b) represent spectra of N=0.35 and N=0.64 melts, respectively.
Table XIV. Raman Frequency Shifts (cm\(^{-1}\)) for GaCl\(_3\):MEIC Melts.

<table>
<thead>
<tr>
<th></th>
<th>N=0.35</th>
<th>N=0.50</th>
<th>N=0.64</th>
<th>N=0.77</th>
</tr>
</thead>
<tbody>
<tr>
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<td>116, m</td>
<td></td>
<td>88, m</td>
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<tr>
<td>345, s, p</td>
<td>345, s, p</td>
<td>150, sh</td>
<td>315, m, p</td>
<td></td>
</tr>
<tr>
<td>376, w</td>
<td>376, w</td>
<td>342, m, p</td>
<td>362, s, p</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>363, s, p</td>
<td>392, m, p</td>
<td></td>
</tr>
</tbody>
</table>

sh: shoulder, w: weak, m: medium, s: strong, p: polarized
(polarized) modes will exhibit much lower intensities when obtained with horizontal polarization.

In order to characterize the data summarized in Table XIV, the vibrational bands may be compared to the assignments made for \( \text{GaCl}_4^- \) and \( \text{Ga}_2\text{Cl}_7^- \) from analyses of various solid and liquid substances containing ionic chlorogallate species. Table XV contains a summary of the vibrational frequencies of the major ionic chlorogallate species whose spectra are available.\(^{94,95}\)

Comparison of the data in Tables XIV and XV demonstrates that melts of neutral to basic melt composition contain the \( \text{GaCl}_4^- \) species. Not only is this the major anionic species present in the \( N=0.35-0.50 \) composition range, but it appears to be the only chlorogallate species present in this composition range. The four absorption bands obtained in this region, readily assigned to \( \text{GaCl}_4^- \), verify tetrahedral symmetry for this species.

Comparison of the data in Table XIV for acidic melts with the frequencies for \( \text{Ga}_2\text{Cl}_7^- \) reported by Oye and Bues for \( \text{CsCl-GaCl}_3 \) melts (Table XV), shows very good agreement.\(^94\) Though there is reasonable agreement with the data of Taylor, it should be noted that his studies in-
Table XV. Raman Vibrational Frequencies (cm\(^{-1}\)) of Known Chlorogallate Species.

<table>
<thead>
<tr>
<th>(GaCl(_4^-))(^94)</th>
<th>(Ga(_2)Cl(_7^-))(^94)</th>
<th>(Ga(_2)Cl(_7^-))(^95)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120, s</td>
<td>90, s</td>
<td>63, vs</td>
</tr>
<tr>
<td>153, s</td>
<td>140, s</td>
<td>107, m</td>
</tr>
<tr>
<td>343, vs, p</td>
<td>266, w, p</td>
<td>141, m</td>
</tr>
<tr>
<td>370, w, sh</td>
<td>316, w, p</td>
<td>284, m</td>
</tr>
<tr>
<td></td>
<td>366, s, p</td>
<td>365, vs</td>
</tr>
<tr>
<td></td>
<td>393, m, sh</td>
<td>407, m</td>
</tr>
</tbody>
</table>

(GaCl\(_3\):CsCl melt) (GaCl\(_3\):CsCl melt) (KGa\(_2\)Cl\(_7\), solid)

45 mol % GaCl\(_3\) 70 mol % GaCl\(_3\)

w: weak, m: medium, s: strong, vs: very strong, sh: shoulder, p: polarized
volved solid KGa$_2$Cl$_7$.\textsuperscript{95} Crystal structure analysis has indicated that solid KGa$_2$Cl$_7$ has the constitution K$^+\text{Ga}_2\text{Cl}_7^-$\textsuperscript{96}. Raman studies of KCl-AlCl$_3$ melts containing GaCl$_3$ gave evidence for the presence of Ga$_2$Cl$_7^-$ with bands at 92, 138 and 366 cm$^{-1}$.\textsuperscript{70} Analysis of a N=0.64 GaCl$_3$:MEIC melt demonstrated that Ga$_2$Cl$_7^-$ was the major anionic species. In addition, the shoulder at 150 cm$^{-1}$ and medium peak at 342 cm$^{-1}$ indicate that GaCl$_4^-$ is present to a lesser extent. It also should be noted that the nature of the cation does not appear to influence appreciably the ion structure. This can be seen by comparing the Raman absorption frequencies of the GaCl$_4^-$ and Ga$_2$Cl$_7^-$ anions for various melt systems (Tables XIV and XV).

Figure 25 contains a Raman spectrum for a N=0.77 chlorogallate melt. The Raman frequency shifts correlate well with the data of Oye and Bues for the Ga$_2$Cl$_7^-$ ion.\textsuperscript{94} Unlike the N=0.64 acidic melt, the Raman spectrum of the N=0.77 melt does not contain any evidence for the presence of the GaCl$_4^-$ ion. In addition, there is no discernible evidence for Ga$_3$Cl$_{10}^-$, though it was hoped that this chlorogallate species might be detected at high melt
FIGURE 25

Raman spectrum of a N=0.77 GaCl₃:MEIC melt.
acidity in this binary system. Further, there is no evidence for the presence of molecular gallium chloride in the N=0.64 and N=0.77 melts, even though its presence similarly could be postulated at high melt acidities.\(^{94}\)

From Raman investigations of room temperature chloroaluminate melts, Gale et al. showed it was possible to assume that the mole fractions of the AlCl\(_4^-\) and Al\(_2\)Cl\(_7^-\) ionic species are proportional, approximately, to the intensity of the strongest bands for each species.\(^{97}\) Similar treatment of the chlorogallate system would indicate that the molar excess of gallium chloride is converted virtually completely to the Ga\(_2\)Cl\(_7^-\) ion at acidities greater than N=0.64 and lower than N=0.77 melt compositions. This is demonstrated by the gradual diminishment of the most intense peak of GaCl\(_4^-\) with increasing melt acidity and its absence in chlorogallate melts of mole fraction greater than N=0.7. In addition, melts of neutral to basic composition did not produce any evidence for the presence of the Ga\(_2\)Cl\(_7^-\) ion.

For the GaCl\(_3\):MEIC melts the predominant equilibrium may be expressed as

\[
2\text{GaCl}_4^- + \text{Ga}_2\text{Cl}_6 \rightleftharpoons 2\text{Ga}_2\text{Cl}_7^- \tag{24}
\]
in accord with the results obtained from Raman investigations. The question of species in acidic melts of acidity greater than \( N = 0.67 \) has still to be resolved and further experimental studies are required to delineate the complexes present. The inability to detect the presence of \( \text{Ga}_3\text{Cl}_{10}^- \) may indicate the presence of competitive equilibria at high melt acidities. Quite possibly, there may exist significant complexation of \( \text{MEI}^+ \) at higher acidities and/or the formation of Lewis acid-base adducts

\[
\text{nR} + \text{GaCl}_3 \rightleftharpoons \text{R:GaCl}_3 + (\text{n-1})\text{R} \rightleftharpoons \text{GaCl}_3(\text{R})_n \quad (25)
\]

where \( \text{R} \) is the organic component in the melt. Conceivably, if the excess Lewis acid does not react with \( \text{Ga}_2\text{Cl}_7^- \), it will react with the next strongest base to free chloride ion in the system, thus precluding formation of \( \text{Ga}_3\text{Cl}_{10}^- \).

4.5 FAST ATOM BOMBARDMENT (FAB) MASS SPECTROMETRY OF CHLOROGALLATE MELTS

Since earlier FAB analyses of chloroaluminate melts (Chapter 3) provided some helpful insights and species identification, FAB analyses of chlorogallate melts were
undertaken to understand better the chemical reactions involved and species present. The Raman studies of these melts demonstrated that ionic chlorogallate species were present to various degrees depending on melt composition. Once again, FAB mass spectrometric analysis seemed ideally suited for investigating the nature of the Ga species present. Negative ion data, in particular, should provide a wealth of information concerning the species which comprise the melts. As was evidenced from analyses of the chloroaluminate melts, results which reflect the chemistry of the condensed phase samples, as a function of changing Lewis acidity, may be obtained.

FAB Analysis of a Basic Chlorogallate Melt

Figure 26 contains a FAB mass spectrum of a N=0.46 GaCl$_3$:MEIC melt. The most intense peak in this spectrum occurs at m/z 211, corresponding to the tetrachlorogallate species. Though the atomic mass unit values correspond very well with theoretical values, the calculated theoretical isotope distribution patterns exhibit peak intensities (for species in the m/z 140-205 range) which differ from experimental results. The discrepancy in peak intensities may possibly be explained in terms of
FAB mass spectrum of a N=0.46 GaCl₃:MEIC melt.
possible monomer/dimer combinations. Existence of such monomer/dimer species would cause overlap of peaks producing a cumulative effect. It has been shown that formation of dimers is typical of halides of boron subgroup elements, with dimerization capacity decreasing with valency decrease. Earlier studies demonstrated that the chloro complexes of subvalent Al species could be detected by FAB analysis and it is reasonable that the chloro complexes of subvalent Ga species also would be detected. Though an oxychloro species of Al was detected in a basic chloroaluminate melt, no corresponding oxychloro or hydroxychloro Ga complexes were found in the FAB spectrum of a basic chlorogallate melt. However, this a limited data set from which to draw conclusive opinions. FAB spectra of melts with deliberately introduced oxide would be of interest.

Another interesting point is the presence of the heptachlorodigallate anion in the FAB spectrum of a basic chlorogallate melt. Raman studies, reported in the previous section, did not show any evidence for $\text{Ga}_2\text{Cl}_7^-$ in a $N=0.35$ basic melt. Even though the cluster appears with a 16% relative intensity, it may not exist in the condensed phase. Quite possibly, the cluster at $m/z$ 387
corresponds to the gas phase reaction of GaCl$_4^-$ combining with the neutral species GaCl$_3$ to produce the Ga$_2$Cl$_7^-$ species. A similar argument may also be used to explain the existence of Al$_2$Cl$_7^-$ ion in the FAB spectra of basic chloroaluminate melts, where it has never been confirmed or postulated to exist by other means in such quantities.

Table XVI contains a summary of the FAB data for a basic chlorogallate melt. Clusters at m/z 141, 176 and 211 corresponding to GaCl$_2^-$, GaCl$_3^-$ and GaCl$_4^-$ clearly indicate chlorocomplexes of Ga in three oxidation states. Both Ga(I) and Ga(III) are well known to exist in the solid, liquid and gas phases. Though the Ga(II) oxidation state compounds are known mostly to exist as gas phase species, some solid phase compounds containing Ga(II) have been reported. Evans et al. prepared the tetra-alkylammonium salts of hexahalogenodigallate(II) ions and confirmed the existence of Ga$_2$Cl$_{6}^{2-}$. Investigations by Beamish et al. showed the existence of neutral complexes of Ga(II) containing Ga-Ga bonds. Subvalent Ga species have been previously detected by mass spectrometry and their detection in these analyses seems to be a product of the FAB environment. However, it should be noted that Ga(I) is stable in room temperature...
Table XVI. Summary of FAB Data for a Basic Chlorogallate Melt.

<table>
<thead>
<tr>
<th>m/z</th>
<th>N=0.46 GaCl₃:MEIC</th>
<th>Relative Intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>141</td>
<td>GaCl₂⁻ (* )</td>
<td>37</td>
</tr>
<tr>
<td>176</td>
<td>GaCl₃⁻ (* )</td>
<td>48</td>
</tr>
<tr>
<td>202</td>
<td>GaCl₃C₂H₂⁻ (* )</td>
<td>38</td>
</tr>
<tr>
<td>211</td>
<td>GaCl₄⁻</td>
<td>100</td>
</tr>
<tr>
<td>316</td>
<td>Ga₂Cl₅⁻</td>
<td>9</td>
</tr>
<tr>
<td>387</td>
<td>Ga₂Cl₇⁻</td>
<td>16</td>
</tr>
<tr>
<td>534</td>
<td>[(GaCl₄⁻)₂MEI⁺]⁻</td>
<td>39</td>
</tr>
</tbody>
</table>

(*) Possible monomer/dimer combination
melts and can be generated electrochemically (Chapter 3). Of further interest is the cluster at m/z 317 which corresponds to \( \text{Ga}_2\text{Cl}_5^- \). Though it is most likely to contain Ga(I) and Ga(III), via combination of a neutral GaCl\(_3\) species with a GaCl\(_2^-\) ion, it may contain the Ga(II) species with an almost equivalent electron density on each gallium atom, i.e., chlorine bridged or Ga-Ga bonded species.

The cluster at m/z 534, corresponding to \([\text{GaCl}_4^-\text{MEI}^+]^-\), is another example of ion association which persists despite the FAB environment. Earlier (Chapter 3), the corresponding tetrachloroaluminate species was reported to occur. Once again, the theoretical isotope distribution pattern confirms the presence of carbon and chlorine atoms in the cluster, i.e., experimental results agree with theoretical isotope predictions. The presence of this cluster provides strong evidence that MEI\(^+\) is the major cationic species in the melt and perhaps indirect evidence of ionic association as ion pairs, triple ions, etc. in the liquid state.
FAB Analysis of Acidic Chlorogallate Melts

FAB mass spectra of two acidic chlorogallate melts are shown in Figures 27 and 28. Figure 27 represents a typical spectrum obtained from an intermediate analysis of a $N=0.58 \text{ GaCl}_3:\text{MEIC}$ sample. Figure 28 contains a FAB mass spectrum of a $N=0.74 \text{ GaCl}_3:\text{MEIC}$ melt. These samples were analyzed in the negative ion mode to determine the type of Ga species present. Analyses of two acidic melts, with significantly different GaCl$_3$ content, were performed to determine if FAB analysis would reflect the different acid-base complex ion chemistry that is believed to occur in the condensed phase.

Qualitatively, the spectrum of the $N=0.74$ melt more closely resembles the spectrum shown for the basic melt than it does the spectrum for the $N=0.58$ melt. In all cases, the most intense peak in each spectrum occurs at $m/z$ 211, corresponding to the tetrachlorogallate species. Interestingly, observation of Figures 27 and 28 shows that the peak intensity of the heptachlorodigallate species at $m/z$ 387 is much weaker for the $N=0.74$ melt. Overall, the spectrum of the $N=0.58$ melt contains more clusters and of greater intensity than the $N=0.74$ melt.
FAB mass spectrum of a N=0.58 GaCl₃:MEIC melt.
FAB mass spectrum of a N=0.74 GaCl$_3$:MEIC melt.
Similar to the FAB spectrum for a basic melt, the FAB spectra of acidic melts contain a cluster at m/z 316, corresponding to Ga₂Cl$_5^-$ . Though this species may or may not contain Ga(II), the cluster at circa m/z 527, presumably corresponding to Ga$_3$Cl$_9^-$ , appears to contain the Ga(II) species. It is to be noted that the spectrum of the N=0.74 melt does not contain a cluster which can be assigned to the Ga$_3$Cl$_{10}^-$ ion.

Table XVII contains a summary of the peak assignments and relative intensities for major clusters in the spectra. Once again, though the resultant peak atomic mass units closely match the theoretical mass values, the relative peak intensities indicate the presence of monomer/dimer combinations at m/z 140-205. Excluding the peak intensity for the tetrachlorogallate species, all peak intensities except for one are greater for the N=0.58 melt than the N=0.74 melt. The relative intensity of the species at m/z 369, corresponding to Ga$_2$Cl$_6$OH$^-$ , is greater in the 0.74 melt. Of further interest in the N=0.74 melt is the absence of a cluster at m/z 533, corresponding to a GaCl$_4^-$/MEI$^+$ triple ion, and the weak intensity of the cluster at m/z 508. In the corresponding N=0.58 melt, clusters of strong intensity occur at
Table XVII. Summary of FAB Spectra of Acidic Chlorogallate Melts.

<table>
<thead>
<tr>
<th>m/z</th>
<th>N=0.58 GaCl$_3$:MEIC$^a$</th>
<th>N=0.74 GaCl$_3$:MEIC$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>141</td>
<td>GaCl$_2^-$ (43)*</td>
<td>GaCl$_2^-$ (9)*</td>
</tr>
<tr>
<td>176</td>
<td>GaCl$_3^-$ (49)*</td>
<td>GaCl$_3^-$ (15)*</td>
</tr>
<tr>
<td>193</td>
<td>GaCl$_3$OH$^-$ (48)*</td>
<td>GaCl$_3$OH$^-$ (39)*</td>
</tr>
<tr>
<td>202</td>
<td>GaCl$_3$C$_2$H$_2^-$ (45)</td>
<td>------</td>
</tr>
<tr>
<td>211</td>
<td>GaCl$_4^-$ (100)</td>
<td>GaCl$_4^-$ (100)</td>
</tr>
<tr>
<td>333</td>
<td>Ga$_2$OCl$_5^-$ (57)</td>
<td>Ga$_2$OCl$_5^-$ (52)*</td>
</tr>
<tr>
<td>369</td>
<td>Ga$_2$Cl$_6$OH$^-$ (73)</td>
<td>Ga$_2$Cl$_6$OH$^-$ (93)</td>
</tr>
<tr>
<td>387</td>
<td>Ga$_2$Cl$_7^-$ (47)</td>
<td>Ga$_2$Cl$_7^-$ (11)</td>
</tr>
<tr>
<td>508</td>
<td>Ga$_3$OCl$_8^-$ (42)</td>
<td>------</td>
</tr>
<tr>
<td>526</td>
<td>obscured by cluster at 533</td>
<td>Ga$_3$Cl$_9^-$ (53)</td>
</tr>
</tbody>
</table>

$a$) Relative intensities (%) in parenthesis.

* Possible monomer/dimer combination.
m/z 508 and 533, corresponding to Ga$_3$OCl$_8^-$ and [(GaCl$_4^-$)$_2$MEI$^+$]$^-$ ion, respectively. It appears more difficult to form triple ions in the vapor phase when a large amount of Ga$_2$Cl$_7^-$ ion is present.

Examination of Tables XVI and XVII reveals that only one organometallic anionic species was detected to an appreciable extent in the FAB analyses. The cluster at m/z 202, assigned to the GaCl$_3$C$_2$H$_2^-$ ion, appears in the FAB spectra of basic and acidic chlorogallate melts. Not surprising, the corresponding Al species, AlCl$_3$C$_2$H$_2^-$, also was detected and can be seen in the chloroaluminate FAB spectra at m/z 158 (Figures 12-16). It should be mentioned that instead of containing the C$_2$H$_2$ group, these organometallic species possibly may contain a cyano group (though it is a less likely fragment of the organic cations).

The clusters at m/z 193 and 369, corresponding to the hydrolyzed gallium species, seem to be related and may reflect condensed phase chemistry. Kinsella et al. have studied the structure of gallium bromides and chlorides, along with their hydrolysis products.$^{101}$ They found that hydrolysis of the trihalides occurred by
splitting the Ga$_2$Cl$_6$ dimer, followed by formation of hydroxylated ions. In the condensed phase, the availability of GaCl$_3$ monomer (via Ga$_2$Cl$_7^-$) is expected to increase with increasing melt acidity. If the FAB analyses reflect the liquid phase chemistry, peak intensities might be expected to be greater for the clusters at m/z 193 and/or m/z 369 for the N=0.74 melt than for the less acidic N=0.58 melt. Though the peak intensity is not larger at m/z 193, the peak intensity is greater for the more acidic chlorogallate melt at m/z 369. Although the GaCl$_3$OH$^-$ ion species intensity is greater for the less acidic melt, as may be the case for the liquid state, the Ga$_2$Cl$_6$OH$^-$ ion species may form by vapor phase association as well as be present in the liquid state.

The only oxide species to occur to an appreciable extent in both acidic melts is Ga$_2$OCl$_5^-$. Though Ga$_3$OCl$_8^-$ occurs to a major extent in the FAB spectrum of the N=0.58 melt, it only appears with a relative intensity of six percent in the FAB spectrum of the N=0.74 melt. A comparison of the FAB spectra for the acidic melts indicates a decreased tendency for oxide formation in the
more acidic chlorogallate melt. Furthermore, a comparison of Tables VI and XVII indicates that Al has a greater tendency to form oxide species than does Ga. In fact, Al exhibits a greater tendency to form dioxychloro and oxyhydroxychloro species than does Ga. However, the chlorogallate FAB spectra obtained lead us to suggest that the gallium chloride is more prone to form stable hydrolyzed products than aluminum chloride.

All of the oxide and hydroxide species in chlorogallate melts have counterparts in the chloroaluminate melts, with the latter having the species $Al_3Cl_6O_2^-$, $Al_3Cl_7O_2H^-$ and $Al_4Cl_9O_2^-$ in addition. Secondary ion mass spectrometric (SIMS) analyses of $AlCl_3$:MEIC melts identified several oxide containing anions, the major ones being identified as $Al_2OCl_5^-$, $Al_2Cl_6OH^-$ and $Al_3Cl_6O_2^-$. The $Al_2OCl_5^-$ ion and the corresponding gallium species have been identified during the present FAB investigations. In addition, FAB analyses have also identified the presence of the $Al_2Cl_6OH^-$ and $Al_3Cl_6O_2^-$ ions, with the former having a corresponding Ga species. The FAB spectra of the respective melt systems reflect liquid phase chemistry in so much as there is a higher tendency for hydrolysis and oxide formation in acidic melts. It
is noteworthy that successive chlorine atom loss by
dissociation was most evident for the highest concentra-
tion species, GaCl$_4^-$ ion, and not for the lesser oxide
and hydroxy species. Unfortunately, the relative extents
of dissociation and association of ion-neutral and
ion-ion fragments are sufficiently difficult to resolve
that the method does not permit estimates of liquid phase
equilibria constants at this stage of its application.
In a recent study of solution equilibrium for the reac-
tion between glycine and Cu(II) in glycerol, the results
showed little correlation between glycerol solution
equilibrium and the observed secondary ions created by
fast atom bombardment. The researchers stated that
one of the reasons for the lack of correlation arises
from FAB induced reactions (i.e. reduction, dehydration
and protonation) which occur in the glycerol solution.
Further studies are required to determine the extent of
similar FAB induced reactions in the analyses of molten
salt systems. Nevertheless, FAB analyses have provided
some helpful insights and generally unambiguous species
identification.
ELECTROCHEMISTRY OF ARSENIC

5.1 INTRODUCTION

Arsenic, which exists in several allotrope forms, occurs approximately half way down the elements in order of abundance. Metallic arsenic, steel-gray colored in the crystalline form, has a melting point of 817°C (28 atm) and sublimes on heating at 618°C. Various arsenic containing minerals are widely distributed throughout nature with small amounts of the free element also being found.

Relatively little is known concerning the electrochemistry of arsenic species in nonaqueous media. Though the electrochemistry of As has received much attention in aqueous media, there exists little data available on the reversibility of electrode processes or on the standard potentials in nonaqueous media. Some studies have been made of AlCl₃-NaCl-KCl melts containing As₂O₃. Yntema and Verdieck, who plated out As from an AlCl₃-NaCl-KCl melt at 156°C, reported the deposition potential to be 0.98 ± 0.04 V versus an Al reference electrode. Electrode potentials of the As(III)/As(0) system (E₀ = -0.46 V versus a Pt reference
electrode) were measured in dilute solutions of the ionic species in a LiCl-KCl eutectic at 450°C. The As(V)/As(III) potential was found to be beyond the potential range of the LiCl-KCl melt. Marquis measured the equilibrium potential of the As(0)/As(III) system in ethyl alcohol and reported the normal potential value to be 0.138 V versus an As electrode.

Though As and its compounds do not appear to have been investigated in NaNO$_3$-KNO$_3$ melts, various arsenates have been studied in fused KNO$_3$ at 350°C. Arsenic and its compounds do not appear to have been studied in fused phosphate or carbonate systems. Since both NaAsO$_2$ and As$_4$O$_6$ separately react with AlCl$_3$-NaCl melts to give volatile AsCl$_3$, there has not been a detailed study of As and its compounds in the AlCl$_3$-NaCl eutectic.

In general, As is deposited from aqueous, acidic and alkaline solutions containing As(III) ions. Good quality As coatings have been deposited with high current efficiency from AsCl$_3$ solutions in acetone. For the present work in the room temperature melts, AsCl$_3$ was chosen as the As species with which to study the electrochemistry of As(III). Though AsCl$_3$ has been
more thoroughly investigated than any of the other arsenic halides, there exists a need for further investigation in nonaqueous media to better understand As(III) reduction\(^{114}\). Information concerning the electrochemical kinetics of As(III) reduction in room temperature melts is vital for evaluating the prospects of GaAs electrodeposition.

### 5.2 ARSENIC SPECIES VOLTAMMETRY

Initial work has involved studying the electrochemistry of As complexes in low temperature AlCl\(_3\):BPC melts using cyclic voltammetry. Figure 29 contains a cyclic voltammogram at scan rates of 20-500 mV/s for As(III) added to an acidic chloroaluminate melt as AsCl\(_3\). It appears that in acidic melts As(III) is reduced by a 3 electron mechanism to As(0) (confirmed by constant potential coulometry, Section 5.3) at circa 0.4 V. At scan rates greater than 200 mV/s, the single reduction peak found at lower scan rates develops a pre-wave shoulder. Arsenic is apparently deposited as a black film from this melt and presumably is removed in the oxidation peak at circa 1.9 V, which possesses a shape characteristic of a stripping peak. Analysis of
CV of approximately 60 mM As(III) at 20, 50, 100, 200 and 500 mV/s, Pt button area 0.810 mm$^2$, in 1.36:1 AlCl$_3$:BPC, 40°C.
the film formed on a Pt electrode was made by differential pulse polarography. Detection of a peak at circa -0.85 V versus SCE, corresponding to the reduction of As(0), was observed upon dissolution of the film in HCl and analysis in a HCl electrolyte.

It should be noted that pure arsenic trichloride is an ampholytic liquid which can accept chloride ions,

$$\text{AsCl}_3 + \text{Cl}^- \rightleftharpoons \text{AsCl}_4^- \quad (26)$$

or donate chloride ions,

$$\text{AsCl}_3 \rightleftharpoons \text{AsCl}_2^+ + \text{Cl}^- \quad (27)$$

In essence, AsCl$_3$ possesses electrical conductivity which has been explained by an autoionization represented by the equation,

$$2\text{AsCl}_3 \rightleftharpoons \text{AsCl}_2^+ + \text{AsCl}_4^- \quad (28)$$

Presumably, the predominant As(III) species in acidic melts is the AsCl$_2^+$ ion, if AsCl$_3$ is a weaker Lewis acid than AlCl$_3$. Previous evidence for the existence of this ion in solutions containing AsCl$_3$ is based on data from conductometric titrations.$^{115,116}$ For the basic region, the predominant As(III) species is
most likely the AsCl$_4^-$ ion. Indirect evidence for the existence of AsCl$_4^-$ ions in AsCl$_3$ solutions has come from conductometric studies, transport number measurements and radiochlorine exchange studies.\textsuperscript{117,118} There exists a need for vibrational spectroscopic studies of these complexes as a function of acidity. Studies of Sb(III) in AlCl$_3$:BPC melts indicated that SbCl$_2^+$ was the major species in the acidic regime, while SbCl$_4^-$ and SbCl$_6^-$ were found to be the dominant species in the basic region.\textsuperscript{119}

With a relatively low specific conductivity at room temperature, arsenic trichloride does not undergo a great deal of self-ionization.\textsuperscript{120} However, in the presence of the ionic chloroaluminate melts, As(III) species most likely coexist in the ionic state. At melt compositions close to the neutral region it is reasonable to expect that AsCl$_2^+$ and AsCl$_4^-$ are present in the melt. Quite possibly, pre-wave shoulders on the major reduction wave, leading to deposition of arsenic, may involve partial reduction intermediates or the presence of several As(III) species.

Table XVIII contains peak potential and peak current data for the voltammograms presented in Figure
Table XVIII. Peak Potential and Peak Current Data for Voltammograms of As(III) in 1.36:1 AlCl₃:BPC.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Scan Rate (mV/s)</th>
<th>(E_{p}^{c}) (V)</th>
<th>(i_{p}) (μA)</th>
<th>(E_{p}^{a}) (V)</th>
<th>(i_{p}) (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~60 mM As(III)</td>
<td>20</td>
<td>0.34</td>
<td>56</td>
<td>1.86</td>
<td>123</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.29</td>
<td>74</td>
<td>1.91</td>
<td>179</td>
</tr>
<tr>
<td>Pt Working Electrode</td>
<td>100</td>
<td>0.25</td>
<td>89</td>
<td>1.95</td>
<td>226</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>0.20</td>
<td>115</td>
<td>2.00</td>
<td>287</td>
</tr>
<tr>
<td>40°C</td>
<td>500</td>
<td>0.14</td>
<td>148</td>
<td>2.07</td>
<td>354</td>
</tr>
</tbody>
</table>
29. As the scan rate is increased, the cathodic peak potentials shift to more negative potentials. In addition, increasing the scan rate causes the anodic peak potentials to shift toward more positive potentials. With respect to the reduction of As(III), the following criteria were used to determine that an irreversible process was involved:

1) peak potential shifts cathodically by 30/n mV for a ten-fold increase in \( \nu \),

2) \( i_p/\sqrt{\nu} \) is constant with scan rate, and

3) there is no current on the reverse scan.\(^7\)

Though anodic currents are obtained on voltammograms, the large difference between the cathodic versus anodic peak potentials (\( \sim 1.6 \) V) indicates irreversibility. Overall, the behavior exhibited in these voltammograms is in closer agreement with irreversible charge transfer than with quasi-reversible charge transfer (Section 3.2, p. 71).

In the neutral region, the electrochemistry of arsenic is much more distinctive. Figure 30 contains cyclic voltammograms recorded at scan rates of 20, 50,
CV of approximately 42 mM As(III) at 20, 50, 100, 200 and 500 mV/s, Pt button area 0.810 mm², in 1.36:1 AlCl₃:BPC, 40°C
100 and 200 mV/s for As(III) in the neutral chloroaluminate melt. The reduction waves are shifted considerably negative from those obtained in an acidic melt and 3 well-resolved peaks are featured on the reverse scan. Once again, a pre-wave shoulder occurs on the major reduction wave. When scanning to potentials near -0.2 V and reversing, two oxidation waves at circa 0.4 and 0.9 V are obtained on voltammograms. Scanning to more negative potentials near -0.5 V and reversing causes the oxidation potentials to shift about 50-100 mV more positive while doubling the anodic currents. It is not until scanning negative past potential circa -0.8 V that a third oxidation wave at about 1.5 V is obtained on the reverse scan of the voltammogram.

Table XIX contains peak potential and peak current data for the voltammograms presented in Figure 30. A discussion of the analyses to quantitatively determine the processes occurring in the neutral regime will be presented in the next section of this chapter. At the present time, it appears that arsenic may be deposited from a neutral melt at circa -0.8 V and the sharp oxidation peak at 1.5 V appears to correspond to the
Table XIX. Peak Potential and Peak Current Data for Voltammograms of a Neutral AlCl$_3$:BPC Melt Containing As(III).*

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Scan Rate mV/s</th>
<th>$E_p^c$, V</th>
<th>$E_p^a$, V</th>
<th>$E_p^{a'}$, V</th>
<th>$E_p^{a''}$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>~42 mM As(III)</td>
<td>20</td>
<td>-0.56 (20)</td>
<td>0.53 (10)</td>
<td>1.13 (12)</td>
<td>1.51 (27)</td>
</tr>
<tr>
<td>Pt Working Electrode</td>
<td>50</td>
<td>-0.62 (29)</td>
<td>0.56 (14)</td>
<td>1.16 (18)</td>
<td>1.53 (45)</td>
</tr>
<tr>
<td>40°C</td>
<td>100</td>
<td>-0.65 (40)</td>
<td>0.58 (22)</td>
<td>1.20 (27)</td>
<td>1.54 (52)</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>-0.68 (56)</td>
<td>0.60 (30)</td>
<td>1.26 (40)</td>
<td>1.55 (58)</td>
</tr>
</tbody>
</table>

*i_p data in parenthesis (μA)
stripping of As deposited at circa -0.8 V. It is quite possible that more than one arsenic species is present initially and that the reduction and oxidation waves correspond to composite behavior and not successive reduction/oxidations of a single species. In addition, the possibility exists that the chloro complexes of the intermediate valence states of arsenic are stable intermediates. Investigations concerning the nature of the reduction/oxidation processes involved in the neutral region will be discussed in the next section of this chapter (5.3).

In basic melt compositions, the voltammetric behavior of arsenic qualitatively is similar to its behavior in acidic media. Figure 31 contains cyclic voltammograms at scan rates of 50, 100 and 150 mV/s for As(III) in a basic chloroaluminate melt. Similar to the voltammograms of As(III) in acidic and neutral melts, there exists a pre-wave shoulder, at circa -0.35 V, prior to the main reduction peak. Presumably, the reduction peak at circa -0.85 V corresponds to the reduction of AsCl$_4^-$ to metallic arsenic.

Table XX contains peak potential and peak current data for the voltammograms of As(III) in a 0.94:1
FIGURE 31

CV of approximately 83 mM As(III) at 50, 100 and 150 mV/s, Pt button area 0.810 mm², in 0.94:1 AlCl₃:BPC, 30°C.
Table XX. Peak Potential and Peak Current Data for Voltammograms of As(III) in 0.94:1 AlCl$_3$:BPC.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Scan Rate (mV/s)</th>
<th>$E_{pc}$ (V)</th>
<th>$i_p$ (µA)</th>
<th>$E_{pa}$ (V)</th>
<th>$i_p$ (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~83 mM As(III)</td>
<td>50</td>
<td>-0.83</td>
<td>34</td>
<td>0.41</td>
<td>68</td>
</tr>
<tr>
<td>Pt Working Electrode</td>
<td>100</td>
<td>-0.86</td>
<td>45</td>
<td>0.42</td>
<td>96</td>
</tr>
<tr>
<td>30°C</td>
<td>150</td>
<td>-0.88</td>
<td>53</td>
<td>0.43</td>
<td>114</td>
</tr>
</tbody>
</table>
As the scan rate is increased, the cathodic peak potentials shift negative. However, the scan rate has less effect on the anodic peak potential. Though the cathodic versus anodic potentials are about 300 mV closer in the basic than the acidic regime, the overall behavior is irreversible in character. It is interesting to note that even though the As(III) concentration is greater in the basic melt, the peak currents are greater in the acidic melt.

Unlike gallium, arsenic may be readily reduced at room temperature in acidic and/or basic chloroaluminate melts. Voltammograms presented thus far in this section demonstrate the significant electrochemical activity of arsenic throughout the acidic, neutral and basic melt compositions. In addition, though As(III) is readily reduced in these melts, oxidation of the metal occurs at potentials approximately one volt more positive than reduction to the metal.

**Voltammetry in Chlorogallate Melts**

Since concurrent studies showed the existence of low temperature chlorogallate molten salt systems, cyclic voltammetric studies were performed with As(III)
in chlorogallate melts. Investigation of As(III), added as AsCl₃, in GaCl₃:MEIC melts was performed to determine if the As(III)/As(0) reduction potential was within the potential window of the melts. Preliminary investigations of this type are required to evaluate the prospects of GaAs film formation from chlorogallate molten salt systems.

Figure 32 contains a cyclic voltammogram of As(III) in a 1.03:1 GaCl₃:MEIC melt. The reference electrode in these studies consisted of a coiled Al wire immersed in a 2:1 AlCl₃:MEIC melt contained within a glass fritted tube. A broad reduction wave (indicative of a slow charge transfer reaction) occurs with a peak plateau at approximately 0.1 V. Upon reversing the scan, a sharp oxidation peak, presumably the As stripping peak, occurs at circa 1.3 V. Once again, similar to its behavior in acidic chloroaluminate melts, As(III) exhibits irreversible behavior. Scanning positive from the rest potential (0.8 V) did not produce any anodic currents other than that expected for the GaCl₃:MEIC melt itself. No oxidation waves which could be assigned to the oxidation of As(III) to As(V) were obtained prior to the positive limit of acidic or basic melts.
CV of approximately 98 mM As(III) at 100 mV/s, Pt button area 0.810 mm$^2$, in 1.03:1 GaCl$_3$:MEIC, 30°C
When employing a Pt working electrode and scanning negative to potentials past 0.0 V in slightly acidic melts, on the reverse scan a Ga stripping peak occurs at circa 0.2 V. Furthermore, scanning negative to circa -0.3 V produces a broad deposition wave together with a stripping peak at circa 0.2 V upon reversal (Figure 33, voltammogram a). However, when glassy carbon is employed as the working electrode different behavior is obtained at the negative limit of acidic melts. Scanning negative to potentials past -0.1 V will produce voltammograms which exhibit sharp deposition peaks (strong reduction currents). However, on the reverse scan hysteresis is observed (Figure 33, voltammogram b). The hysteresis exhibited in this case is typical of that noted for nucleation overvoltage deposition processes.

With the previous observations having been presented, the following observations of voltammograms of acidic chlorogallate melts containing As(III) will be mentioned. Upon scanning negative to -0.4 V (Pt working electrode) and reversing, no Ga stripping peak is observed (Figure 34, voltammogram a). However, a very large oxidation peak, presumably the As stripping peak, occurs at circa 1.4 V. Quite possibly, the As film
FIGURE 33

CV's at 100 mV/s of a 1:1:1 GaCl₃:NEIC melt, (a) Pt working electrode and (b) glassy carbon working electrode, 30°C.
CV's of a 1.03:1 GaCl₃:MEIC melt containing approximately 98 mM As(III) at 100 mV/s, employing Pt working electrode, (a), and glassy carbon working electrode, (b), 30°C.
possesses a sufficiently high electrical resistivity to suppress Ga deposition. In the case of the voltammograms where glassy carbon is used as the working electrode, a sharp deposition peak occurs at circa 0.1 V with hysteresis observed on the reverse scan (Figure 34, voltammogram b). The hysteresis on the reverse scan most likely involves an arsenic nucleation overvoltage deposition process followed by an oxidation at circa 1.4 V. The anodic wave at circa 1.4 V most likely corresponds to an arsenic stripping peak. No further analyses of these surface films were attempted.

As reported earlier, neutral chlorogallate melts possess wider electrochemical windows than either acidic or basic chlorogallate melts. Figure 35 contains a cyclic voltammogram of As(III) in a neutral GaCl₃:MEIC melt. The effect of repeated cycling to more negative potentials is clearly shown in this figure. The main cathodic peak, presumably As deposition, occurs at -0.75 V. In general, scanning to more negative potentials will, upon reversal, cause the anodic peaks to shift toward more positive potentials while producing larger anodic currents. Except for the case of scanning to -1.5 V, the charge under the cathodic reduction peaks
CV of approximately 93 mM As(III) at 150 mV/s, repeated cycling to more negative potentials, Pt button area 0.810 mm², in 1:1 GaCl₃:MEIC, 30°C.
is approximately equal to the charge under the anodic stripping peaks. The anodic peak currents range in intensity from 60 µA to 345 µA for the cyclics progressing to negative potentials of -0.1 V to -1.5 V, respectively.

The voltammetric behavior of As in basic chlorogallate media qualitatively is similar to its behavior in acidic media. Arsenic deposition occurs at approximately -0.7 V while a stripping peak, presumably that of As, occurs on the reverse scan at circa 0.4 V.

Voltammetric investigations in chloroaluminate and chlorogallate melts indicate that As(III) exhibits irreversible behavior. In addition, arsenic may be readily reduced at room temperature in chloroaluminate and chlorogallate melts. No matter what the system or melt composition, voltammograms of melts containing As(III) demonstrate the significant electrochemical activity of arsenic. Also, no oxidation waves which could be assigned to the oxidation of As(III) to As(V) were obtained prior to the positive limit of acidic or basic melts (chloroaluminate/chlorogallate).
5.3 CONSTANT POTENTIAL COULOMETRY

Constant potential coulometric investigations were performed to determine the number of electrons involved in the electrochemical reduction of As species. Coulometric experiments were carried out by changing the potential from a value where no current (other than background) passed to one where the desired reaction was expected to occur. Selection of a suitable potential was made from cyclic voltammetry data. Electroactive arsenic species were depleted during electrolysis with the measured current-time integration providing the number of coulombs involved. Electronic integration by the EG&G 273 Potentiostat provided accurate coulometric determination of electroactive As species analyzed in acidic, neutral and basic chloroaluminate melts. Reference electrodes contained melts of 2:1 molar composition.

Coulometry in an Acidic Melt

Electrolysis at a constant potential of 0.25 V of a 1.4:1 AlCl$_3$:BPC melt containing forty microliters of AsCl$_3$ was performed to confirm the expected As(III) to As(0) reduction. A glassy carbon crucible doubled as a
container and large area working electrode to accelerate reduction of As(III) from the stirred melt. The results of this coulometric experiment confirmed that As(III) was reduced by a 3 electron mechanism to As(0). Experimentally, electrolysis at 0.25 V yielded a charge of 124 coulombs corresponding to a n value of 2.7 electrons (theory value for the charge for n=3 is 138 coulombs). Reasonable agreement of the experimental n value with the theoretical value indicates that the main cathodic peak in Figure 29 involves As deposition (coulometry in room temperature molten salts is difficult experimentally because of background impurities and/or volatile species).

Coulometry in a Neutral Melt

Investigations concerning the nature of the reduction/oxidation processes involved in the neutral region have been performed. It was felt that coulometric studies would help explain the distinctive electrochemical behavior of As(III) in a neutral melt. Initial work involved constant potential electrolysis of a neutral AlCl₃:BPC melt containing fifty microliters of AsCl₃. Electrolysis at a constant potential of -0.6 V
produced a 151 coulomb charge accumulation prior to reduction of currents to background level. In this case, a 3 electron reduction corresponds to approximately 173 coulombs (theory value). When the applied potential was reset to -0.8 V, the current overload indicator came on after accumulation of a few coulombs. Examination of the melt showed that the melt was no longer clear and colorless but cloudy greyish-black. In addition, a dark film was observed on the area of the crucible which had been in contact with the melt.

Some investigations concerning the nature of As species in neutral melts were performed in neutral AlCl₃:MEIC melts. Electrolysis was begun at a constant potential of -0.25 V. Before moving to a constant potential of -0.5 V, 137 coulombs of charge were accumulated. Figure 36 contains cyclic voltammograms of a neutral AlCl₃:MEIC melt containing 0.187 g of AsCl₃ before, (a), and after partial electrolysis, (b). If the main reduction peak corresponds to a 3 electron reduction of As(III), a charge accumulation of about 300 coulombs would be expected. Whereas the pre-wave shoulder prior to the main reduction peak is not well defined for the neutral AlCl₃:BPC melt (Figure 30), a
well defined shoulder at circa -0.2 V occurs on the main reduction peak in the neutral MEIC based chloroaluminate melt. Figure 36 (b) contains a voltammogram of a neutral melt after 186 coulombs of electrolysis. Comparison of the voltammograms before electrolysis and after partial reduction shows a significant reduction in electrochemical activity, most likely signifying As(III) deposition onto the carbon crucible or reduction to a non-electroactive arsenic species. Further electrolysis at a potential of -0.6 V resulted in the accumulation of another 95 coulombs before the current subsided to background level. The charge accumulated to this point corresponds to a n value of 2.8 electrons, perhaps indicating reduction of the As(III) to As(0).

After several hours of further electrolysis a cyclic voltammogram, shown in Figure 37, was taken. Besides the lack of cathodic waves until circa -1 V, the voltammogram exhibits a shift in acidity, to the basic regime, from the previous voltammograms (Figure 36). Apparently, the electrolysis has had the effect of producing a sufficient amount of free chloride ions to cause an imbalance in the melt neutrality. This shift in melt acidity is not surprising considering the
CV's of a 1:1 AlCl₃:MEIC melt containing As(III), before, (a), and after partial reduction, (b), Pt working electrode, 100 mV/s, 30°C.
CV at 100 mV/s indicating a shift in melt acidity during reduction of As(III) in a 1:1 AlCl₃:MEIC melt, Pt working electrode, 40°C.
fragile balance required to maintain a neutral melt. The shift to the basic regime presumably results from nearly complete deposition of As and/or reduction of the chlorocomplexes of arsenic ions to noncomplexed As species. In the present case, the production of free chloride ions is sufficient to shift the melt acidity to the basic regime. The shift of the neutral melt to the basic regime also was noticed in subsequent coulometric studies of As(III) reduction in neutral melts. Conversely, if significant diffusion of the reference melt into the bulk melt occurred, the melt acidity would shift from the neutral to the acidic regime.

A difficulty encountered in these studies arose from trying to reduce As(III) past the elemental state. Constant potential electrolysis at potentials more negative than -0.7 V met with current and/or potential overload signals because of the high electrical resistivity of As (33 μohm-cm). In some experiments, a charge was accumulated which theoretically corresponded to an additional one electron reduction past the metallic state. Some codeposition of AlAs or other insoluble/soluble subvalent As species might be
responsible, but no fixed conclusions could be drawn from these coulometric measurements.

**Coulometry in a Basic Melt**

Lastly, some coulometric investigations were made to explore As(III) species reduction in basic chloroaluminate melts. Studies performed in acidic and neutral melts revealed that high As(III) concentrations were detrimental to coulometric investigations. Thus, to minimize problems encountered upon the reduction of As(III) to As(0), i.e. high electrical resistivity upon As deposition, smaller concentrations of As(III) were used. Studies of As(III) were carried out in basic melts (20-30 g) which contained less than 100 mg of AsCl₃. Preliminary studies showed that electrolysis of As(III) in a basic melt, at a constant potential circa -0.8 V, corresponded to a 3 electron reduction. Deposition onto Pt foils at -0.6 and -0.8 V produced silvery-gray and blackish-gray films, respectively. Analysis of these films by X-ray fluorescence confirmed the presence of arsenic.

Constant potential electrolyses of basic melts containing As(III) usually were performed in a carbon
crucible which served as the working electrode. Figure 38 contains voltammograms of a 0.88:1 AlCl₃:MEIC melt to which 0.104 g of AsCl₃ had been added. The top voltammogram, (a), was obtained after As(III) addition and prior to electrolysis. Reversal just after the first cathodic peak (circa -0.88 V) results in the presence of an oxidation peak at 0.4 V, which presumably is the As stripping peak. However, scanning negative to potentials past -1.45 V (potential of second cathodic peak) produces negligible anodic currents upon the reverse scan prior to the solvent oxidation. The second reduction peak is truly irreversible in character.

The middle voltammogram, (b), of Figure 38 was obtained after partial reduction (accumulation of two-thirds of the theoretical charge for As(III) to As(0) reduction). Electrolysis at -0.85 V yielded an experimental n value of 3.2 electrons. Constant potential electrolysis was continued at -1.1 V, before ending at -1.4 V with current and potential overloading of the system occurring. In Figure 38, the bottom voltammogram, (c), was taken after ceasing electrolysis. Theoretically, the electrolysis proceeded through a 4 electron reduction of As(III).
CV's of a 0.88:1 AlCl₃:MEIC melt at 100 mV/s, C(WE), 40°C: after AsCl₃ addition, (a); after partial reduction of As(III), (b); and after electrolysis was ceased, (c).
Constant potential coulometry employing Pt crucibles as the working electrode were performed with results similar to those described above. Voltammetry on glassy carbon in basic melts shows two significant and nearly equal reduction waves (Figure 38, voltammogram a) prior to the negative limit of the MEIC based melts. However, the apparent high electrical resistivity of As precluded definitive identification of the negative oxidation state(s) of arsenic species in the melt. More success in identifying the intermediates may result by generating As species from As(0) by oxidation with coulometric and/or spectroscopic analyses and solubility studies.

5.4 FAST ATOM BOMBARDMENT (FAB) MASS SPECTROMETRY OF CHLOROALUMINATE MELTS CONTAINING AsCl₃

Since prior FAB analyses of molten salts (reported in this work) had provided helpful insights and species identification, the technique was used to investigate chloroaluminate melts containing added As(III). Samples were once again analyzed in the negative ion mode to examine the nature of the species present. A fresh 1.5:1 AlCl₃:MEIC melt (0.793 g) was prepared and 34 mg
of AsCl$_3$ added. In addition, 90 mg of AsCl$_3$ was added to a freshly prepared 0.86:1 AlCl$_3$:MEIC melt (0.714 g).

Approximately one microliter samples of the 1.5:1 and 0.86:1 chloroaluminate melts were analyzed separately and portions of the resultant FAB mass spectra (90-350 amu) are shown in Figure 39. The FAB mass spectra obtained are very similar to those obtained for the melts themselves. It should be noted that after the probe was removed a reddish-black deposit was observed on the Cu probe tip. Apparently, the AsCl$_3$ reacted with the Cu sample holder forming a deposit which could presumably diminish the prospects for detection of As(III) negative ions in the melt samples. Comparison of the spectra in Figure 39 with the spectra in Figures 13 and 14 shows that they are similar except for a cluster at m/z 295 in Figure 39 (b).

A summary of the FAB spectra, for the chloroaluminate melts containing AsCl$_3$, which are partially shown in Figure 39 is presented in Table XXI. Analyses of the basic and acidic melts did not yield any clusters at m/z 340 or greater with a relative intensity greater than six percent. Comparison of the data in Table XXI with the data in Tables VI and VII shows they are very
FAB mass spectra of a 1.5:1 AlCl₃:MEIC melt containing AsCl₃, (a), and a 0.86:1 melt containing AsCl₃, (b). (Cu probe tip)
Table XXI. Summary of FAB Spectra of Chloroaluminate Melts Containing As(III) (Cu Probe Tip).

<table>
<thead>
<tr>
<th>m/z</th>
<th>1.5:1 AlCl₃:MEIC*</th>
<th>0.86:1 AlCl₃:MEIC*</th>
</tr>
</thead>
<tbody>
<tr>
<td>132</td>
<td>-----</td>
<td>AlCl₃⁻ (10)</td>
</tr>
<tr>
<td>149</td>
<td>AlCl₃OH⁻ (8)</td>
<td>-----</td>
</tr>
<tr>
<td>158</td>
<td>AlCl₃C₂H₂⁻ (7)</td>
<td>AlCl₃C₂H₂⁻ (26)</td>
</tr>
<tr>
<td>169</td>
<td>AlCl₄⁻ (100)</td>
<td>AlCl₄⁻ (100)</td>
</tr>
<tr>
<td>247</td>
<td>Al₂OCl₅⁻ (76)</td>
<td>Al₂OCl₅⁻ (16)</td>
</tr>
<tr>
<td>283</td>
<td>Al₂Cl₆OH⁻ (51)</td>
<td>-----</td>
</tr>
<tr>
<td>295</td>
<td>-----</td>
<td>AlAsCl₅O⁻ (22)</td>
</tr>
<tr>
<td>301</td>
<td>Al₂Cl₇⁻ (6)</td>
<td>Al₂Cl₇⁻ (48)</td>
</tr>
<tr>
<td>325</td>
<td>Al₃Cl₆O₂⁻ (63)</td>
<td>-----</td>
</tr>
<tr>
<td>449</td>
<td>-----</td>
<td>[(AlCl₄⁻)₂MEI⁺]⁻ (12)</td>
</tr>
<tr>
<td>458</td>
<td>Al₄Cl₉O₂⁻ (45)</td>
<td>-----</td>
</tr>
</tbody>
</table>

*Relative intensities (%) in parenthesis
similar. All the major clusters in the spectra for the melts containing AsCl$_3$ except one can be attributed to Al species. The cluster at m/z 295 presumably corresponds to an AlAsCl$_5$O$^-$ ion. Quite possibly, this ion forms from the combination of a neutral AsCl$_3$ species with an AlCl$_2$O$^-$ ion. None of the expected major As species, AsCl$_4^-$ or AsCl$_6^-$, appear to manifest themselves in the spectra. Particularly from m/z 90-350, only one peak cluster of greater than two percent (relative intensity) appears to correspond to an As species. From m/z 350-700 almost all the peak clusters possess a relative intensity less than five percent and are found in spectra of the melts without added AsCl$_3$.

Though the Cu probe tip was never analyzed, the melt did react visibly with the probe indicating that Cu was an inappropriate material for a probe tip in these studies. The vials containing the melts were placed back into the glove box until a more suitable probe tip could be used. Two months later, after a suitable stainless steel probe tip could be machined, the vials were once again removed for FAB analyses. Figure 40 contains FAB mass spectra of the previously described acidic and basic chloroaluminate melts. Qualitatively,
FAB mass spectra of a 1.5:1 AlCl₃:MEIC melt containing AsCl₃, (a), and a 0.86:1 melt containing AsCl₃, (b). (Stainless steel probe tip)
the spectra in Figure 40 are similar to the spectra in Figure 39. It is quite surprising again that no major peak cluster corresponding to a simple As ion species appears in these spectra considering that FAB analyses of Ga(III) in the chloroaluminate melts produced a cluster at m/z 211 (GaCl$_4$\(^-\) with a 60-70% relative intensity, Section 3.5). Once again, a cluster at m/z 295 appears in the spectra of the basic melt containing As(III). Inspection of the probe tip did not indicate any type of reaction between As(III) and the stainless steel.

Table XXII contains a summary of the FAB spectra of the chloroaluminate melts containing AsCl$_3$, obtained when using a stainless steel probe tip. Once again, the species detected are similar to those expected upon FAB analyses of the melts themselves (Tables VI and VII). Comparison of the data in Tables XXI and XXII indicates that the species found in melts were not altered appreciably from a brief exposure to the atmosphere. The data once again reflects some of the overall chemistry of the melts, but the inability to identify more than one As species suggests that further investigations are necessary to understand the As acid/base and redox
Table XXII. Summary of FAB Spectra of Chloroaluminate Melts Containing As(III) (Stainless Steel Probe Tip).

<table>
<thead>
<tr>
<th>m/z</th>
<th>1.5:1 $\text{AlCl}_3:\text{MEIC}^*$</th>
<th>0.86:1 $\text{AlCl}_3:\text{MEIC}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>97</td>
<td>$\text{AlCl}_2^-$ (4)</td>
<td>$\text{AlCl}_2^-$ (12)</td>
</tr>
<tr>
<td>132</td>
<td>$\text{AlCl}_3^-$ (2)</td>
<td>$\text{AlCl}_3^-$ (13)</td>
</tr>
<tr>
<td>149</td>
<td>$\text{AlCl}_3\text{OH}^-$ (7)</td>
<td>$\text{AlCl}_3\text{OH}^-$ (3)</td>
</tr>
<tr>
<td>158</td>
<td>$\text{AlCl}_3\text{C}_2\text{H}_2^-$ (8)</td>
<td>$\text{AlCl}_3\text{C}_2\text{H}_2^-$ (21)</td>
</tr>
<tr>
<td>169</td>
<td>$\text{AlCl}_4^-$ (100)</td>
<td>$\text{AlCl}_4^-$ (100)</td>
</tr>
<tr>
<td>247</td>
<td>$\text{Al}_2\text{OCl}_5^-$ (51)</td>
<td>$\text{Al}_2\text{OCl}_5^-$ (8)</td>
</tr>
<tr>
<td>283</td>
<td>$\text{Al}_2\text{Cl}_6\text{OH}^-$ (43)</td>
<td>-----</td>
</tr>
<tr>
<td>295</td>
<td>-----</td>
<td>$\text{AlAsCl}_5\text{O}^-$ (26)</td>
</tr>
<tr>
<td>301</td>
<td>$\text{Al}_2\text{Cl}_7^-$ (2)</td>
<td>$\text{Al}_2\text{Cl}_7^-$ (27)</td>
</tr>
<tr>
<td>325</td>
<td>$\text{Al}_3\text{Cl}_6\text{O}_2^-$ (12)</td>
<td>-----</td>
</tr>
<tr>
<td>449</td>
<td>-----</td>
<td>$[(\text{AlCl}_4^-)_2\text{MEI}^+]^-$ (4)</td>
</tr>
<tr>
<td>459</td>
<td>$\text{Al}_3\text{Cl}_9\text{O}_2^-$ (5)</td>
<td>-----</td>
</tr>
</tbody>
</table>

*Relative intensities (%) in parenthesis
chemistry. For example, daughter ion measurements of the As species, tentatively assigned as an (AlCl₂O·AsCl₃)⁻ ion, would confirm its identity as a thermodynamically stable Lewis acid-base adduct.

The one significant difference, between the spectra of previous melts and the present spectra of melts with As(III), involves a cluster circa m/z 295 in the spectra of basic melts containing AsCl₃. This cluster appears to possess an isotopic pattern characteristic of five chlorine atoms being present and has tentatively been assigned to an AlAsCl₅O⁻ ion species. However, because of the overlap with the cluster at m/z 301 unequivocal species assignment is complicated. A study of the daughter ion of the species at m/z 295 would be helpful. It would be quite informative to analyze the melts containing AsCl₃ in the positive ion mode (using the stainless steel probe tip). Though more hazardous, FAB analyses of AsCl₃ and MEIC mixtures in the positive and negative ion modes could prove to be beneficial in identifying ionic As species.
6.1 INTRODUCTION

Gallium arsenide is a semiconducting material of immense interest with diverse applications. Since current device fabrication techniques waste a tremendous portion of the starting raw materials, methods which offer more efficient disposition of materials warrant investigation. Theoretically, electrochemical methods of deposition have the advantage of precise control of layer thickness, which would enable economical usage of materials. Though electrochemical deposition may not at this time produce materials of semiconductor grade purity, prospects for low cost photovoltaic application seem feasible.

DeMattei et al. demonstrated that molten salt electrodeposition of GaAs was possible. Deposition onto Ni and GaAs substrates occurred at 720-760°C from a molten solution containing NaAsO₂ and Ga₂O₃ in a B₂O₃-NaF solvent. Electrodeposition of GaAs at 300°C has been observed under galvanostatic conditions by Tremillon and coworkers. Deposition was achieved on Au electroplated Ni electrodes from a KGaCl₄ melt.
containing AsI₃. The inherent advantage of working at lower temperatures would be to reduce problems caused by the volatility of many arsenic species. This suggested the evaluation of low temperature molten salts for thin film fabrication of GaAs. Utilization of molten salts with GaCl₃ and AsCl₃ to produce GaAs would significantly reduce the risks and losses encountered in present preparative methods.

Investigations of the electrochemical behavior of gallium and arsenic species by various techniques (e.g. coulometry, potentiometry and voltammetry) have been performed. In this chapter, studies concerning mixtures of GaCl₃ and AsCl₃ in chloroaluminate melts will be presented. Prospects for electrochemically forming layers of GaAs from room temperature chloroaluminate melts are discussed. In addition, prospects for the utilization of chlorogallate melts for thin film fabrication of III-V compounds will be briefly addressed.

6.2 VOLTAMMETRY OF CHLOROALUMINATE MELTS CONTAINING AsCl₃ AND GaCl₃

Cyclic voltammetry has been used to study the electrochemical behavior of chloroaluminate melts
containing mixtures of As(III) and Ga(III). The individual electrochemical behavior of Ga(III) and As(III) in chloroaluminate melts has been investigated and reported earlier in this work. Cyclic voltammetric analyses of mixtures of Ga(III) and As(III) should provide valuable information concerning the qualitative prospects for codeposition as molecular GaAs. In addition, voltammetric studies may indicate the effect, if any, that gallium and arsenic exhibit on each others respective reduction/oxidation characteristics (i.e. redox potentials).

**Voltammetry in AlCl$_3$:BPC Melts**

Initial studies centered on mixtures of As(III) and Ga(III) in acidic AlCl$_3$:BPC melts. The main reason for concentrating studies on acidic melts was the apparent inability to reduce basic gallium complexes. Slow Ga(III) reduction kinetics relative to As(III) reduction led to investigations using a large excess of GaCl$_3$ over AsCl$_3$. Figure 41 contains several voltammograms, of Ga(III) and As(III) in a 1.82:1 AlCl$_3$:BPC melt, scanning progressively more cathodic. As the voltage was scanned to increasingly more negative potentials past the first
CV of approximately 153 mM Ga(III) with 6 mM As(III) at 200 mV/s, scanning progressively more cathodic, Pt button area 0.810 mm$^2$, 1.82:1 AlCl$_3$:BPC, 40°C.
reduction peak (~0.9 V), a single oxidation peak at about 1.6 V shifted positive slightly and split into a double wave. In addition, when scanning to potentials more negative than 0.2 V, a third oxidation peak at circa 1.2 V occurs.

The behavior exhibited by the mixture of AsCl$_3$ and GaCl$_3$ in an acidic chloroaluminate melt, as shown in Figure 41, warrants further inspection. Scanning negative will produce a reduction wave at approximately 0.9 V and upon reversal an oxidation peak at circa 1.6 V (Figure 41 (a)). Scanning further negative to 0.3 V will produce upon reversal a second oxidation peak at about 1.75 V (Figure 41 (b)). When scanning even more negative to 0.1 V, a third oxidation wave at 1.15 V occurs (Figure 41 (c)) with the magnitude of the anodic currents for the peaks at circa 1.61 and 1.75 V being approximately equal at this scan rate. Upon scanning to 0.0 V, the magnitudes of the anodic peaks at 1.21 and 1.78 V increase while the anodic current for the peak at 1.62 V remains fairly constant (Figure 41 (d)).
the cyclic voltammograms in Figure 41, the following observations may be made:

1) the species reduced at about 0.9 V forms a product that is apparently oxidized at circa 1.6 V,

2) a species (or chemical follow-up product) formed by reduction upon scanning to potentials more negative than 0.4 V is oxidized at about 1.7-1.8 V, and

3) the product from the species reduced at 0.2-0.0 V, potentials just prior to Al deposition, is oxidized at approximately 1.2 V.

As reported earlier (Tables III and XVIII), Ga(III) multi-electron reduction occurs at approximately 0.9 V while As(III) reduction occurs at circa 0.3 V in acidic AlCl_3:BPC melts. In Figure 41, the first reduction wave occurs in the area of Ga(III) to Ga(I) reduction. However, the oxidation peak on the reverse scan occurs at a potential uncharacteristic of any gallium species when only GaCl_3 is added to a melt (Section 3.2). The second reduction wave, which occurs between potentials 0.5 and 0.2 V, may represent reduction of As(III) with a characteristic stripping peak occurring on the reverse
scan at circa 1.75 V. Presumably, the reduction occurring between 0.3 and 0.1 V involves Ga(I), with the corresponding oxidation wave at circa 1.18 V involving Ga(0) or Ga(I) oxidation.

To assist in the characterization of the oxidation peaks, anodization of an ion beam sputtered GaAs film was performed in a 1.9:1 AlCl₃:BPC melt. The GaAs film (nominal 50 Å thickness) had been coated onto a Mo substrate. Upon scanning positive from the rest potential (0.65 V), two waves appeared at circa 1.85 and 1.95 V, prior to melt oxidation. Figure 42 contains a cyclic voltammogram of an initial scan in the direction of the positive limit of the melt at a relatively slow scan rate, 20 mV/s. Though the second oxidation wave is not as well defined as the wave at 1.85 V, the anodic currents are very strong for both waves.

Considering that the GaAs film formally involves gallium in the +3 oxidation state and arsenic in the -3 oxidation state, the oxidation waves most likely involve arsenic species. In its +3 oxidation state, Ga(III) can be oxidized no further. However, As(-3) may be oxidized to As(0) which may then be oxidized to As(+3).
CV depicting the anodization of a GaAs film, Mo foil substrate, at 20 mV/s, in a 1.9:1 AlCl₃:BPC melt, 30°C.
following mechanism may explain the occurrence of the two oxidation waves in Figure 42

\[ \text{As}(-3) \rightarrow \text{As}(0) + 3\text{e}^- \quad (29) \]

followed by

\[ \text{As}(0) \rightarrow \text{As}(+3) + 3\text{e}^- \quad (30) \]

With respect to the voltammograms in Figures 41 and 42, there appears to be an implication that a chemical reaction occurs between the Ga and As species while electrochemical reduction of Ga(III) and As(III) is being performed. Several hypotheses may be presented to account for the formation of GaAs (vide infra):

1) recombination of elemental gallium and arsenic

\[ \text{Ga}(\text{III}) + 3\text{e}^- \rightarrow \text{Ga}(0) \quad (31) \]
\[ \text{As}(\text{III}) + 3\text{e}^- \rightarrow \text{As}(0) \quad (32) \]
\[ \text{Ga}(0) + \text{As}(0) \rightarrow \text{GaAs} \quad (33) \]

2) reaction of Ga(I) with As(III)

\[ \text{Ga}(\text{III}) + 2\text{e}^- \rightarrow \text{Ga}(I) \quad (34) \]
\[ \text{Ga}(I) + \text{As}(\text{III}) + 4\text{e}^- \rightarrow \text{GaAs} \quad (35) \]

3) reaction of Ga(I) with As(0)

\[ \text{Ga}(\text{III}) + 2\text{e}^- \rightarrow \text{Ga}(I) \quad (36) \]
\[ \text{As}(\text{III}) + 3\text{e}^- \rightarrow \text{As}(0) \quad (37) \]
\[ \text{Ga}(I) + \text{As}(0) + \text{e}^- \rightarrow \text{GaAs} \quad (38) \]
However, the precise nature of the mechanism for the formation of GaAs is unclear and further work is needed to understand the reaction steps of the forward (deposition) and reverse (anodization) mechanisms.

**Voltammetry in AlCl₃:MEIC Melts**

Additional studies were performed on mixtures of As(III) and Ga(III) in basic and neutral AlCl₃:MEIC melts. The MEIC based system was used because of its expanded electrochemical window in the neutral and basic regimes. With a several hundred millivolt expansion in the ranges of the electrochemical windows, additional electrochemical behavior may be observed.

To an approximately 0.86:1 AlCl₃:MEIC melt was added 21 microliters of AsCl₃. A series of cyclic voltammograms were obtained to study the behavior of arsenic species between 0.8 and -2.1 V, prior to GaCl₃ addition to the melt. For the sake of comparison, three voltammograms of As(III) in the basic AlCl₃:MEIC melt are shown in Figure 43. The voltammograms depict the effect of scanning progressively more negative from the rest potential of 0.25 V. Two reduction waves at circa
CV's of approximately 20 mM As(III) at 100 mV/s, scanning progressively more negative, in a 0.86:1 AlCl$_3$:MEIC melt, W working electrode, 30°C.
-0.3 and -1.1 V are resolved. Scanning to more negative potentials prior to reversal firstly has the effect of causing a single oxidation peak to split into two peaks, and then the disappearance of the more positive anodic peak (Figures 43 (b) and (c)).

After obtaining a set of voltammograms with AsCl₃ in the basic melt, GaCl₃ was added to study the electrochemical behavior of the mixture. Figure 44 contains cyclic voltammograms of a mixture of GaCl₃ and AsCl₃ in a basic chloroaluminate melt. On scanning to -1.3 V before reversal, two reduction waves occur at potentials similar to those reported for voltammograms in Figure 43. The major difference is that after the oxidation peak at circa 0.3 V splits into two waves, in the case of Figure 44, both waves remain following progressively more negative scans. It is interesting to note that the first oxidation wave (at about 0.15 V) becomes smaller after the initial split, while the second oxidation peak becomes larger with progressively more negative scans. Possibly due to slow kinetics for Ga(III) reduction and overshadowing by As(III) reduction currents, no reduction waves appear to correspond to reduction of a gallium species. It is difficult to determine from
CV's of As(III) and Ga(III) in a 0.86:1 AlCl₃:MEIC melt, scanning progressively more negative, 100 mV/s, W working electrode, 28°C.
voltammetric studies alone the effect that Ga(III) addition has on the electrochemistry of As species.

Further studies were made to investigate mixtures of AsCl$_3$ and GaCl$_3$ in neutral AlCl$_3$:MEIC melts. Neutral AlCl$_3$:MEIC melts possess an electrochemical window of over 4 V which allows for the study of various redox species over a relatively large potential range. Within this potential range, the voltammetric behaviors of Ga(III) and As(III) in the neutral AlCl$_3$:MEIC melt are qualitatively similar to their behaviors in an acidic AlCl$_3$:BPC melt. However, on scanning to about -2 V (the negative limit of the neutral melt), an additional reduction peak at -0.2 V along with a previously unobserved oxidation wave at 2.1 V occur (Figure 45.)

Figure 45 contains cyclic voltammograms of As(III) and Ga(III) scanning progressively more cathodic. Scanning negative to 0.5 V will upon reversal produce a sharp oxidation peak at 1.7 V. When scanning to 0.0 V and reversing two oxidation waves occur at circa 1.8 and 1.95 V. Reduction of a gallium complex, presumably GaCl$_4$\(^-\), occurs at about -0.2 V with the oxidation wave at about 1.35 V appearing after reversing at -0.5 V.
CV's of a neutral AlCl$_3$:MEIC melt containing As(III) and Ga(III), scanning progressively more negative, 100 mV/s, W working electrode, 25°C.
Addition of GaCl$_3$ to a neutral melt produced larger cathodic currents at -0.2 V with a corresponding increase in the charge accumulated for the peak at circa 1.35 V on the positive sweep. Scanning negative to -1.0 V does not produce any additional reduction peaks, but it does cause the oxidation peak at about 1.8 V to begin to split into two distinct peaks. The bottom voltammogram in Figure 45 clearly shows four distinct oxidation waves. Previously, only three oxidation peaks had been obtained in voltammograms for mixtures of As(III) and Ga(III) in acidic AlCl$_3$:BPC melts.

It appears that only the reduction peak at -0.2 V and the oxidation peak at 1.35 V directly involve gallium species. However, it should be noted that broad waves, involving underlying chemistry, may be concealed in the present investigations. Presumably, the first oxidation wave at about 1.35 V corresponds to the oxidation of Ga(I) or Ga(0) to Ga(III), while the remaining oxidation peaks involve arsenic species. Quite possibly, the oxidation peaks at approximately 1.8 and 1.9 V (potentials similar to those observed for the anodization of the GaAs film) involve the oxidation of a sub-valent As species along with As(0). In addition,
the oxidation peaks at 1.8 and 1.9 V may indicate the slow formation of GaAs on the negative scan. Most likely, the peak at circa 2.1 V corresponds to the oxidation of As(III) to As(V). Though not clearly seen, a similar oxidation wave may occur in BPC based melts. However, due to the proximity of this potential to the positive limit of acidic and neutral AlCl₃:BPC melts, a possible As(III) to As(V) oxidation wave would be overshadowed by melt oxidation leading to chlorine evolution.

6.3 ELECTRODEPOSITION STUDIES

With the groundwork studies completed, research efforts were directed toward producing GaAs films by codeposition at, or near, room temperature. A series of experiments were performed to establish the prospects of producing GaAs films in chloroaluminate melts. Codeposition experiments were performed in acidic AlCl₃:BPC melts and neutral AlCl₃:MEIC melts. Platinum foils were used as the deposition substrates. Only preliminary results of X-ray fluorescence (XRF) analyses will be discussed in this section. A complete discussion of analyses of electrodeposited films will be presented
after an overall view of the electrodeposition studies has been developed.

**Electrodeposition in Acidic AlCl$_3$:BPC Melts**

Electrodeposition studies were performed with a 1.6:1 AlCl$_3$:BPC melt containing approximately five times the amount of AsCl$_3$ as GaCl$_3$. Current densities between 2 and 8 mA/cm$^2$ were employed with deposition potentials between 0.77 to 0.20 V. Various Pt foils were used with the temperature controller being set at 40°C. When analyzed by XRF, only films obtained at potentials between approximately 0.5 to 0.2 V produced peaks other than the Pt background. Unfortunately, potentiostatic deposition produced films rich in As only. Figure 46 contains a representative XRF spectrum with peaks at the following 20 angles (LiF): 30.5° and 34.0°, which confirms the presence of arsenic, and 32.3° and 38.1°, due to the Pt foil substrate.

Next, a 1.64:1 AlCl$_3$:BPC melt was prepared and an approximately equimolar amount of AsCl$_3$ and GaCl$_3$ added. Deposition was performed with c.d.s of 5-6 mA/cm$^2$ at 40°C. Potentials for deposition were set between 0.6 and 0.45 V over a period of several hours. XRF analyses
FIGURE 46

XRF spectrum of an electrodeposited As film on a Pt foil substrate.
revealed that films deposited on Pt foils under these conditions were rich in arsenic.

In studies with excess As(III) and/or equimolar amounts of As(III) and Ga(III), a trend of always producing films rich in As was established. This trend in electrodeposition studies, along with voltammetric behavior, made it apparent that slow kinetics for Ga(III) reduction relative to As(III) was problematic. In addition, the role of temperature in compound formation could be more significant than expected or hoped.

The next investigations were performed in melts of higher acidity (i.e. 1.8:1 AlCl$_3$:BPC) that contained an excess of GaCl$_3$ over AsCl$_3$. Film formation was attempted from a 1.82:1 AlCl$_3$:BPC melt with the GaCl$_3$ concentration being approximately twenty times greater than the AsCl$_3$ concentration. Using c.d.s of 0.5-2 mA/cm$^2$, while employing potentials between 0.9-0.5 V, produced yellowish-brown to silver films. XRF studies failed to detect the presence of Ga or As. Switching to potentials between 0.4-0.2 V at c.d.s of 0.2-1 mA/cm$^2$ produced brownish-grey films. In addition to peaks due to the presence of Pt and As, a small peak at 35° and a shoulder at 39° (possibly confirming Ga) were observed.
on XRF spectra of films deposited at the lower potentials. Thus, it appeared that excess GaCl₃ concentrations along with potentials more negative than previously used would be required for codeposition.

Further deposition studies were performed in a 1.82:1 AlCl₃:BPC melt (19.3 g) containing 0.40 g GaCl₃ and 0.086 g AsCl₃ at 40°C. With the Ga(III) concentration being approximately five times greater than that of As(III) and employing potentials near the potential of Al deposition, it was hoped that more favorable results would be obtained. Films deposited at potentials between 0.2-0.05 V with c.d.s less than or equal to 1 mA/cm² were greyish-black in color. Characterization of the films, deposited on Pt foils, by XRF established the presence of arsenic and gallium. A representative XRF spectrum, shown in Figure 47, contains peaks due to arsenic and gallium along with the Pt foil substrate. The peaks at 35° and 38.9° correspond to the presence of gallium while the peaks at 30.5° and 34.1° correspond to the presence of arsenic. In view of the utilization of potentials near the potential of Al deposition, the question of whether or not films could be produced free of Al would have to be addressed. However, in this
XRF spectrum of an electrodeposited film containing Ga and As on a Pt foil substrate. (Degrees 2θ) (Thin Film)
section only the determination of the major elemental constituents will be addressed. A more detailed characterization of films containing gallium and arsenic will be presented in Section 6.4.

To further establish the necessary conditions for codeposition, a series of experiments were performed in 1.7:1 to 1.9:1 AlCl₃:BPC melts. Deposition potentials in the range of 0.25-0.0 V with c.d.s of 0.1-10 mA/cm² were examined. Gentle stirring of the melts, with temperatures regulated at 40-45°C, prevented deposition of grossly malformed films. Deposition times typically ranged from 2-18 hours depending on the As(III) and Ga(III) concentrations and the extent of deposition desired.

A typical electrodeposition study will be presented for illustrative purposes. It involved the use of a 1.8:1 AlCl₃:BPC melt (16.2 g) containing 0.61 g GaCl₃ and 0.09 g AsCl₃. Initially, the melt was light yellow in color, but turned a yellowish-brown after the electrodeposition of four films. The first Pt foil was placed in the melt and electrodeposition performed at -0.15 V with a c.d. of approximately 2 mA/cm². After several hours the first Pt foil was removed and a second
Pt foil placed in the melt. A thin film was electrodeposited with potentials being gradually raised from -0.1 V to 0.2 V with c.d.s of 1-2.5 mA/cm² over a period of several hours. A third Pt foil replaced the second Pt foil in the melt and the potential set at -0.2 V with the temperature controller (previously set at 40°C) being turned off. Once again, a period of several hours of electrodeposition passed before removing the Pt foil and placing a new foil in the melt. Electrodeposition at 0.2 V was carried out for a 24 hour period at a c.d. of 2.5 mA/cm² and 40°C.

Table XXIII contains a summary of the XRF analyses for the study described in the preceding paragraph. The first two Pt foil substrates contained codeposited gallium and arsenic. Figure 48 contains a XRF spectrum from the analysis of the first electrodeposited film. Surprisingly, Pt foils 3 and 4 were electrodeposited with sufficiently thick Ga films that the substrate itself was weakly detected. It appears that the As(III) concentration was depleted after the second electrodeposition experiment. Subsequent studies, where more than one film was to be electrodeposited, involved periodic AsCl₃ addition to avoid As(III) depletion.
# Table XXIII. Summary of Spectra for Films Electrodeposited in a 1.8:1 AlCl₃:BPC Melt.*

<table>
<thead>
<tr>
<th>Pt Substrate</th>
<th>Peaks Observed (2θ angles in degrees, LiF)ₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>38.9 (Ga), 38.2 (Pt), 34.1 (As), 32.1 (Pt), 35.1 (Ga) and 30.6 (As)</td>
</tr>
<tr>
<td>2</td>
<td>39.0 (Ga), 38.1 (Pt), 34.1 (As), 34.8 (Ga), 32.3 (Pt) and 30.6 (As)</td>
</tr>
<tr>
<td>3</td>
<td>39.0 (Ga), 34.9 (Ga) and 34.1 (As)</td>
</tr>
<tr>
<td>4</td>
<td>38.9 (Ga), 35.0 (Ga), 34.2 (As), 32.3 (Pt) and 30.6 (As)</td>
</tr>
</tbody>
</table>

* Melt initially contained 0.09 g AsCl₃ and 0.61 g GaCl₃ (c.d.s of 1-3 mA/cm²)

ₓ Arranged in descending order of relative intensity
XRF spectrum of an electrodeposited film containing Ga and As on a Pt foil substrate. (Degrees 2θ) (Thick Film)
Additional studies confirmed that codeposition was favored by the use of potentials just prior to Al deposition, low current densities and a Ga(III) concentration 2-5 times greater than the As(III) concentration.

**Electrodeposition in a Neutral AlCl₃:MEIC Melt**

Electrodeposition experiments were performed under potentiostatic conditions at room temperature in neutral AlCl₃:MEIC melts. The neutral melts contained 20-40 microliters of AsCl₃, with the Ga(III) concentration being at least five times greater than the As(III) concentration. Deposition potentials were between 0.1 and -1.0 V with current densities ranging from 1 to 10 mA/cm². XRF analyses of the deposits on Pt foil substrates indicated that As and Ga could be codeposited in neutral AlCl₃:MEIC melts at room temperature. Initial XRF scans were problematic due to the inability to clearly resolve the major peaks for Pt (substrate) and Ga. In addition, the intense peak at 34°, corresponding to As, overshadowed detection of a minor peak at 34.9°, expected for the presence of Ga. To overcome this difficulty, the film was partially removed by mechanical
means and adhered to a piece of scotch tape for XRF analysis. Figure 49 contains a XRF spectrum for an electrodeposited film (-0.8 V, 25°C) adhered to the tape. The two major peaks at about 38.9° and 34.1° indicate the presence of gallium and arsenic, respectively. Unfortunately, due to the shutdown of the X-ray diffraction unit for safety related repairs the composition of the films, i.e. molecular GaAs or Ga(0) and As(0), could not be ascertained further. Once again, extreme experimental care was required to maintain the delicate balance of a neutral melt. Small amounts of AsCl₃ and GaCl₃ were used to minimize deposition effects related to the production of free chloride ion in the melt.

Prospects of Codeposition from Chlorogallate Melts

Film formation from a chlorogallate melt would eliminate aluminum codeposition/contamination problems. Utilization of a chlorogallate melt, in theory, would reduce the variables involved in codeposition investigations. Electrochemical studies (Section 4.3) have indicated that reduction of an acidic chlorogallate melt involves Ga deposition. Recent studies have shown that
FIGURE 49

XRF spectrum of a film electrodeposited in a 1:1 AlCl₃:MEIC melt containing AsCl₃ and GaCl₃.
deposition of Ga occurs from a basic GaCl$_3$:MEIC melt at 80°C upon melt reduction. In addition, reduction of chlorogallate species may produce Ga(I) species in the melt. Cyclic voltammetry of AsCl$_3$ in chlorogallate melts (Section 5.2) has indicated that As(III) is amenable to reduction in the melts. Several factors, including their thermal stability to at least 125°C, suggest further investigation of the chlorogallate melts for thin film fabrication of gallium based III-V materials.

6.4 CHARACTERIZATION OF ELECTRODEPOSITS

Electrodeposited films, produced under potentiostatic conditions in acidic melts, with the Ga(III) concentration greater than the As(III) concentration, were analyzed by various methods. X-ray fluorescence was used to determine the major elemental constituents of the films. To determine if films containing Ga and As were indeed GaAs, X-ray powder diffraction (XRD) was performed. Electron dispersive scattering (EDS) analysis of a film on Pt foil was used to examine major and minor elemental constituents. Analysis by Inductively
coupled plasma (ICP) assisted also in detection of major and minor constituents of films.

**XRF Analyses**

After a film had been electrodeposited, the Pt foil substrate was removed from the melt and rinsed with toluene and acetone. Before any other type of analysis was performed, XRF analysis of the film was performed to determine the major elemental constituents. The scanning range was typically 28°-40° (2θ). This range was of particular interest since the major peaks, corresponding to fluorescence lines, for As, Ga and Pt occur between 30°-39°. If XRF analysis did not indicate the presence of Ga and As, efforts returned to electrodeposition studies. However, if Ga and As were detected, one or more of the previously mentioned analytical techniques were performed.

If Ga and As were present in a sample, peaks corresponding to the fluorescence lines of Ga and As, would be observed in a XRF spectrum at the following 2θ angles (LiF): 34.91° and 38.92° (Ga), and 30.45° and 34.00° (As). Figure 50 contains an XRF spectrum of a p-GaAs crystal. The peaks observed at 34.9° and 38.9°
FIGURE 50

XRF spectrum of a p-GaAs crystal.
confirm the presence of Ga, while the peaks at 30.5° and 34.0° correspond to the presence of As. Films usually were analyzed on the Pt foil substrate and this sometimes introduced problems. The peaks for Pt occur at 32.3° and 38.1° and, unfortunately, the Pt peak at 38.1° usually overshadowed the Ga peak at 38.9°.

Films electrodeposited at potentials above 0.3 V and/or with excess As(III) in the melt produced films rich in As (Figure 46). When films were electrodeposited at potentials more negative than 0.3 V (i.e. near the potential of Al deposition), XRF analyses determined the presence of Ga and As (Figures 47 and 48). Since the XRF spectrum in Figure 48 corresponds to a thicker film, it is less affected by the Pt foil substrate than the spectrum in Figure 47. In addition, the relative peak intensities in Figure 48 are proportioned similar to those in Figure 50 (GaAs crystal).

A few general observations can be made from the visual examination of films analyzed by XRF. Films determined to contain only As were black or dark-grey in color. Silvery-grey films when analyzed by XRF usually contained codeposited Ga and As, while silver colored films were found to be rich in Ga. Microscopic
examination of codeposited films revealed that lower current densities and gentle stirring during electro-deposition minimized dendritic formation of deposits. In addition, nodular deposits usually occurred at sites of surface defects on the Pt foils.

**EDS and ICP Analyses**

While XRF and XRD (discussion to follow) analyses were used to confirm the major constituents of films, their compositions were verified by EDS and ICP analyses. The main reason for the selection of EDS and ICP is their ability to detect trace impurities in the films. It should be noted that EDS is a non-destructive technique which allows further investigation of the film. However, ICP is a destructive technique which involved mechanical removal of the film and dissolution in a concentrated acid prior to analysis.

Analysis of a film on a Pt foil by EDS confirmed the presence of Ga and As. Figure 51 contains an EDS spectrum obtained after analysis of a film which previously had been found to contain Ga and As (from XRF analysis). Peak energies at 2.08 and 9.43 keV correspond to the presence of the Pt foil. The presence
FIGURE 51

EDS spectrum of a film containing codeposited Ga and As on a Pt foil substrate.
of Ga and As was verified by peaks at 1.10 and 1.31 keV, respectively. In addition, peaks believed to be due to the presence of Si (1.75 keV) and Cl (2.63 keV) were also observed. The Si peak may be a result of the melt etching the glass vessel used during electrodeposition, or the film coming in contact with various glass vessels during transfers and becoming contaminated. The presence of chloride ion in the film may be due to insufficient rinsing of the film and/or occlusion in the film during electrodeposition. Once again, the Pt foil substrate produces peaks which overshadow peaks of interest. Most likely, similar to the case of XRF studies, thicker electrodeposited films would increase the Ga and As peaks while decreasing the intensity of Pt peaks due to the foil substrate.

Representative films were occasionally analyzed by ICP. In general, XRF studies were performed to determine that the films contained codeposited Ga and As prior to ICP analysis. Dissolution of films in nitric acid followed by ICP analysis showed that Ga and As were the two major components. Though no Si was detected, trace amounts of Al and Fe were detected. Iron is a known contaminant in AlCl₃ and its detection may imply
the occlusion of some melt in the deposited film, or that trace amounts of Fe were deposited. Though EDS did not confirm the presence of Fe or Al, it did detect the presence of chloride ion. Thus, it appears that the results from EDS and ICP analyses indicate trace amounts of impurities in codeposited films. However, use of carbon or teflon vessels (container for melt), higher quality AlCl₃ and improved film rinsing techniques would significantly reduce the level of trace impurities in electrodeposited films.

**XRD Analyses**

Previous analyses confirmed the presence of codeposited Ga and As. If the deposit was crystalline, X-ray diffraction would determine if indeed the films were GaAs. However, if the X-ray powder diffraction studies did not provide evidence for crystalline GaAs, the possibility of an amorphous GaAs film still existed.

Analysis of a crystalline material will yield peaks at characteristic 2θ angles which can be related to the interplanar distances. The relationship between the wavelength of the X-ray beam (λ), the angle of
diffraction ($\theta$), and the interplanar distance of the crystal is given by the Bragg Equation,

$$n\lambda = 2d \sin \theta$$  \hspace{1cm} (39)

where $n$ represents the order of diffraction. For the present analyses the wavelength of the X-ray beam is 1.5413 Å (Cu K\textsubscript{\alpha}) while $n=1$. Substitution of the numerical values for $n$ and $\lambda$ allows simplification of Equation 39,

$$\frac{0.7706 \, \text{Å}}{\sin \theta} = d$$  \hspace{1cm} (40)

Thus, analysis of a film would yield characteristic diffraction angles and allow the calculation of $d$. Table XXIV contains $d$ spacings for selected materials of interest in the present study.

For calibration purposes an ion beam sputtered GaAs film (50 Å thickness) which had been coated onto a Mo substrate was analyzed. Surprisingly, 20 diffraction angles (LiF) at 40.6°, 58.6° and 73.8° ($d = 2.22, 1.57$ and 1.28 Å, respectively), corresponding to Mo, were obtained. Since the GaAs film was relatively thin, the sensitivity of the X-ray powder diffraction unit is apparently not high enough to detect such films. Next,
Table XXIV. Interplanar Distances for Selected Inorganic Crystals.

<table>
<thead>
<tr>
<th>Crystalline Material</th>
<th>d spacings (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.83, 0.90, 0.93, 1.17, 1.22, 1.43, 2.02 and 2.34</td>
</tr>
<tr>
<td>As</td>
<td>1.12, 1.73, 1.88, 2.24, 2.72, 2.74, 3.48 and 5.44</td>
</tr>
<tr>
<td>Ga</td>
<td>1.25, 1.79, 1.96, 2.00, 2.26, 2.92, 2.95 and 3.83</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.89, 1.09, 1.15, 1.30, 1.14, 1.70, 2.00 and 3.26</td>
</tr>
<tr>
<td>Mo</td>
<td>0.00, 0.84, 0.91, 1.00, 1.11, 1.28, 1.57 and 2.22</td>
</tr>
<tr>
<td>Pt</td>
<td>0.81, 0.87, 0.90, 1.13, 1.18, 1.39, 1.96 and 2.26</td>
</tr>
</tbody>
</table>
films determined to contain codeposited Ga and As were analyzed. Analysis of films on Pt foil substrates usually produced the following 20 diffraction angles: 39.8°, 46.2°, 67.6° and 81.5°. Once again, the results obtained corresponded to the substrate.

To circumvent the problem of the analysis of a thin film on a substrate, electrodeposited films were removed by mechanical means. In general, due to difficulties in alignment of the sample, several films were combined for X-ray powder diffraction analyses. Analysis of the powder, obtained by mechanical removal of films, typically produced a strong peak at 27.3° and a weak peak at 45.2° (occasionally with a very weak peak at 53.7°). A partial spectrum from a typical XRD analysis is shown in Figure 52. The results obtained in this and similar analyses are consistent with the major peaks found in the diffraction pattern of crystalline GaAs. Unlike the high temperature result obtained by Tremillon and coworkers, no diffraction lines due to As were observed. Unfortunately, the shutdown of the X-ray diffraction unit for safety related repairs seriously impeded further progress in studies dealing with optimizing film quality. However, the XRD analyses showed
FIGURE 52

XRD spectrum of films, electrodeposited from acidic AlCl$_3$:BPC melts, containing GaAs.
(Degrees 2θ)
that crystalline GaAs could be electrodeposited from an acidic AlCl$_3$:BPC melt.
CONCLUSIONS

The electrochemistry and complex ion chemistry of Ga is similar to that of aluminum in chloroaluminate melts, except Ga(I) is stable. Potentiometric analyses of Ga(I) ion, produced by anodization in an acidic AlCl₃:BPC melt, gave \( E_{\text{Ga(I)/Ga(0)}} \) equal to 0.339 V versus Al (2:1) reference and one-electron Nernst slope. Potentiometry of Ga(I) species indicates that \( \text{GaCl}_2^- \) ion may be the predominant lower valence Ga(I) species in the basic regime, while little dependence of Ga(I) was found on melt acidity in the acidic regime. Slow electron transfer kinetics were found in the case of Ga(III) reduction. Deposition of Ga at room temperature could be obtained from acidic chloroaluminate melts containing GaCl₃.

Arsenic (III) reduction appears to involve irreversible charge transfer in the chloroaluminate melts. Voltammetric and coulometric studies revealed that As(III) is amenable to reduction to As(0) in acidic, basic and neutral melts. Coulometric investigation of As(III) reduction past the elemental state proved problematic, presumably due to the high electrical resistivity of As. Voltammetric studies of As(III) in
chlorogallate melts have indicated that As(III) exhibits irreversible behavior.

Fast atom bombardment (FAB) mass spectrometric analyses of chloroaluminate melts, with and without added GaCl$_3$ and AsCl$_3$, have provided valuable insights and species identification. Anions such as AlCl$_4^-$, Al$_2$Cl$_7^-$, GaCl$_4^-$ and AlAsCl$_5$O$^-$ were detected along with subvalent species such as AlCl$_2^-$ and AlCl$_3^-$. In addition, various oxychloro and hydroxychloro species of Al were identified; they include AlCl$_3$OH$^-$, Al$_2$OCl$_5^-$, Al$_2$Cl$_6$OH$^-$, Al$_3$Cl$_6$O$_2^-$ and Al$_3$Cl$_8$O$^-$. Further FAB studies of melts containing AsCl$_3$, especially in the positive ion mode, would be beneficial. Results obtained reflect the chemistry in the condensed phase as well as gas phase reaction products.

Investigations of the electrochemical behaviors of Ga and As species had revealed that Ga and As can each be electrodeposited from acidic melts. With Ga(III) concentrations 2-5 times greater than the As(III) concentration, codeposited films were obtained under potentiostatic conditions from acidic AlCl$_3$:BPC and neutral AlCl$_3$:MEIC melts. X-ray Fluorescence, Electron Dispersive Scattering and Inductively Coupled Plasma
analyses of films showed that the major film atomic constituents were gallium and arsenic. X-ray Diffraction analyses demonstrated that codeposited films contained crystalline GaAs. Further work is required to develop methods to optimize film quality and to evaluate their prospect for practical solar energy photocell applications.

Characterization of novel low temperature melts based on GaCl$_3$, by Differential Scanning Calorimetry (DSC), electrochemical, FAB and Raman studies, have been performed. Solid-liquid phase transition data have been obtained by DSC for the GaCl$_3$:BPC and GaCl$_3$:MEIC molten salt systems. Cyclic voltammetric studies revealed that the electrochemical windows for the chlorogallate melts are a few hundred millivolts narrower than the corresponding chloroaluminate melts. Various chlorocomplex anions, such as GaCl$_2$\textsuperscript{-}, GaCl$_3$\textsuperscript{-}, GaCl$_4$\textsuperscript{-}, Ga$_2$Cl$_5$\textsuperscript{-} and Ga$_2$Cl$_7$\textsuperscript{-} were detected during FAB analyses of the chlorogallate melts. In addition, FAB studies detected the presence of analogous oxychloro and hydroxychloro species to those of Al; they include GaCl$_3$OH$^-$, Ga$_2$OCl$_5$\textsuperscript{-}, Ga$_2$Cl$_6$OH$^-$ and Ga$_3$OCl$_8$\textsuperscript{-}. Raman studies of the GaCl$_3$:MEIC melts have demonstrated that the ionic chlorogallate
species, $\text{GaCl}_4^-$ and $\text{Ga}_2\text{Cl}_7^-$, are present in accord with an anticipated acid-base equilibrium. Several factors, including the thermal stability of chlorogallate melts to at least 125°C, suggest that further investigations should be made of these melts for prospective use in thin film fabrication of Ga based III-V materials.
REFERENCES


VITA

Steven Paul Wicelinski was born on March 5, 1960, in Derby, Connecticut. He attended Fairfield College Preparatory School and graduated in 1977. Upon graduation, he was awarded a four year, full tuition Headmaster Scholarship to attend Fairfield University. In 1981, he received a Bachelor of Science degree in Chemistry from Fairfield University.

The author entered the graduate school of Louisiana State University, Baton Rouge in August 1981. While attending LSU, he presented a paper at the Fifth International Symposium on Molten Salts in Las Vegas, Nevada, and attended the NATO Advanced Study Institute on Molten Salt Chemistry in Camerino, Italy. He was awarded an U. S. Air Force Graduate Student Summer Fellowship to perform research at the U. S. Air Force Academy in 1986. Mr. Wicelinski is presently a candidate for the degree of Doctor of Philosophy at LSU.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

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Major Field: Chemistry

Title of Dissertation: "GaAs Film Formation from Low Temperature Chloroaluminate Melts"

Approved:

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