GALLIUM SPECIES ELECTROCHEMISTRY IN ROOM TEMPERATURE CHLOROALUMINATE Melts

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ABSTRACT

Constant potential and current electrolyses have been used to study Ga(I) ions in room temperature chloroaluminate melts. A potentiometric analysis of Ga(I) ion, produced by anodization in 1.5:1 mole fraction AlCl₃:1-butylpyridinium chloride (BPC) system, 35°C, gave E° Ga(I)/Ga(0)=+0.339 V vs. Al(2:1) reference and one-electron Nernst slope. Potentiometry of Ga(I) species, produced by anodization and by reduction of added GaCl₃, as a function of melt acidity, indicates that GaCl₂⁻ ion may be the predominant lower valence gallium species in the basic regime. Little, if any, dependence of Ga(I) was found on melt acidity at acidic melt compositions. Deposition of Ga(0) was possible from acidic but not basic melts. A small voltammetric wave, assigned to Al underpotential deposition on Ga, is reported for slow scans in acidic melts. Prospects for depositing pure films of the compound semiconductor GaAs are discussed briefly.

INTRODUCTION

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 (1). Verdieck and Yntema reported that solutions of Ga(III) in an AlCl₃-NaCl-KCl molten eutectic at 156°C showed a reduction process at +0.83 V and deposition at about +0.2 V vs. Al reference electrode (2). Anders and Plambeck have investigated the electrochemistry of Ga in an AlCl₃-NaCl-KCl melt at 135°C (3). Using potentiometric and voltammetric techniques, they demonstrated that chloroaluminate melts favored the existence of the lower valence Ga(I) ionic species more than aqueous media 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 (4). Tremillon and coworkers have investigated the acidobasic properties of molten potassium tetrahalogenogallates (5). They reported that molten tetrahalogenogallates were chemically similar to tetrahalogenoaluminates, however, the existence of the Ga(I) lower oxidation state complicated the determination of melt acidity. More recently, von...
Barner has reported the results of potentiometric investigations of the complex formation of Ga(III) in KCl-AlCl₃ melts at 300°C (6).

As part of an investigation of the prospects of electrodepositing films of the commercially important III-V semiconductor gallium arsenide, of useful quality, we have attempted to better understand the electrochemistry of gallium species in room temperature chloroaluminate melt systems (7). GaAs films have potential applications for high efficiency solar cells cf. (8,9) or other semiconductor devices.

EXPERIMENTAL

Preparation of melts and equipment for cyclic voltammetry have been reported elsewhere (7). Constant potential and current electrolyses were made with cells in a dry box under a purified argon atmosphere. 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. 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. Electrolyses were usually with stirred melts containing less than 75 mg of electroactive species. Crystalline, anhydrous GaCl₃ of 99.999% purity (Aesar) was obtained in sealed ampoules and used as received. Constant current coulometry was performed with a Brinkman (ES24) coulostat. Gallium working electrodes were prepared from ingots of Ga metal of 99.99% purity (Alfa). A Keithley 179 TRMS digital voltmeter was used for potentiometric measurements.

RESULTS AND DISCUSSION

Potentiometric Investigations

In order to understand better the formation and stability of Ga(I) ion species in low temperature melts, constant potential and current electrolyses were performed on acidic melts. Earlier cyclic voltammetric measurements had shown that an exhaustive (theoretical) two-electron reduction depleted the melt entirely of Ga(III) species, added as GaCl₃, thereby allowing electrochemical or spectroscopic examinations of the Ga(I) ion species (7). It has been reported previously that Ga(III) species in a KCl melt at 300°C could not be reduced directly to Ga(0) (5). 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 (10). In low temperature basic chloroaluminate melts, it was not possible to reduce the Ga(I) species prior to reduction of the butylpyridinium cation, e.g., cyclic voltammetric studies did not produce current...
responses for Ga(I) species (produced by constant potential electrolysis and added to a basic melt). Thus, attempts to electrodeposit gallium in basic melts, similar to the chloride system, were unproductive. In our voltammetric studies of Ga(III) species in low temperature chloroaluminate melts, glassy carbon, tungsten and platinum working electrodes were employed. However, the best electrochemical responses were achieved at platinum. Thus, similar to the case for Al in acidic and basic chloroaluminates, it appears that Ga may be deposited from acidic gallium species but not from the basic complexes which form in the presence of an excess of Cl\textsuperscript{−} ion in these systems.

Anodization of a pure gallium electrode can be used to determine the standard reduction potential, \( E_0 \), of the Ga(I)/Ga(0) couple. The Nernst plot, shown in Figure 1, was obtained by varying the Ga(I) activity, produced by anodization of Ga at low current densities in a 1.5:1 AlCl\textsubscript{3}:BPC melt, and measuring the emf of the Ga(I)/Ga(0) half-cell vs. Al(2:1) reference electrode. The least squares slope was calculated to be 59 ± 2 mV (theory value for \( n = 1 \) at 35°C is 61 mV) and the intercept value for the standard electrode potential on the mole fraction scale is \( E_0 = 0.339 \pm 0.005 \) V vs. Al (2:1) reference. This value may be compared to the \( E_0 \) value of 0.199 V obtained at 135°C for Ga(I)/Ga(0) in a ternary AlCl\textsubscript{3}-NaCl-KCl melt (3). No corrections for liquid junction potentials (likely insignificant), nor reference electrode temperature differences are available.

The form of the Ga(I) ion species also may be studied with potentiometry by varying the Lewis acidity (Cl\textsuperscript{−} ion activity) of the melt. Note that the above Nernst plot of Ga(I)/Ga(0) was uncorrected for any melt acidity change for the Ga(I) ion mole fraction range 3.27 \( \times 10^{-4} \) to 2.04 \( \times 10^{-2} \). Such a correction requires a knowledge of the competitive equilibria with free melt Cl\textsuperscript{−} ion in the acidic regime and the implicit assumption is that the Ga(I) is essentially noncomplexed. Potentiometric titrations of AlCl\textsubscript{3}:BPC melts containing a fixed Ga(I) mole fraction were performed by addition of BPC. The potentiometric measurements involving the Ga(I)/Ga(0) couple were carried out using the cell formally depicted by

\[
\text{Al}\,(2:1)\,\text{AlCl}_{3}:\text{BPC}|fritted\,disk|\text{AlCl}_{3}:\text{BPC},\,\text{Ga(I)}|\text{Ga(0)}
\]

Emf measurements were made versus an Al (2:1) reference as a function of melt composition with a high impedance voltmeter. Typical data are illustrated in Figure 2. It may be noted that in the acidic composition range the Ga(I) ion potential is practically unaffected by the melt acidity which may mean that Ga(I) is noncomplexed 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 GaCl\textsubscript{m}\textsuperscript{(m−)} was considered in the basic composition regime. Information concerning the identity and stability of these complex ions can be obtained by curve fitting basic melt titration data to the

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expression

\[ E = E_0 + \frac{RT}{F} \ln X_{\text{GaCl}_m^{1-m}} + \frac{RT}{F} \ln K - \frac{mRT}{F} \ln X - E_j \]

where the equilibrium constant, \( K \), is defined by

\[ K = \frac{X_{\text{Ga(I)}} (X_{\text{Cl}^-})^m}{X_{\text{GaCl}_m^{1-m}}} \]

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

\[ E = E_0 + \frac{RT}{F} \ln a_{\text{Ga(I)}} \]

using the standard electrode potential and assuming that the activity of \( \text{Ga(I)} \) approximates the mole fraction of \( \text{Ga(I)} \). Representative data associated with the ion mole fractions for the potentiometric titration of \( \text{Ga(I)} \) are contained in Tables I and II. Analysis of the potentiometric titration data indicated that \( \text{Ga(I)} \) is complexed mainly as \( \text{GaCl}_2^- \) ion in the basic melt.

Table I contains data obtained after the reduction of \( \text{Ga(III)} \) to \( \text{Ga(I)} \) in an initial 1.5:1 \( \text{AlCl}_3: \text{BPC} \) melt. The data contained in Table II was obtained after the anodization of a gallium electrode in a 1.25:1 \( \text{AlCl}_3: \text{BPC} \) melt, to produce \( \text{Ga(I)} \). Figure 3 contains a plot of \( E \) vs. \( \log X_{\text{Cl}^-} \) constructed from the data shown in Tables I and II (indicating a second-power dependence on chloride ion). For the basic emf values obtained from Table I, a graph of emf vs. \( \log X_{\text{Cl}^-} \) gave a line of slope 0.110 ± 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 II, plotted in Figure 3, is 0.106 ± 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 \( \text{Cl}^- \) ion mole fraction might arise from an inadequate model or the presence of adventitious oxidants. The presence of these oxidants caused difficulties in obtaining accurate emf values, however, it is reasonable to infer from these results that \( \text{GaCl}_2^- \) ion is the predominant species in the basic regime.

Voltammetric Investigations

As mentioned above, platinum proved to be the best substrate electrode material for resolving voltammetric waves. Unfortunately, as reported earlier (7), even with platinum, the reduction waves \( \text{Ga(III)}/\text{Ga(I)} \) and \( \text{Ga(I)}/\text{Ga(0)} \) had quasi-reversible characteristics and showed evidence of complications as a function of acidity in the 1:1 to 2:1 melt composition range.

Cyclic voltammetric studies also have been performed using \( \text{AlCl}_3:1\text{-methyl-3-ethylimidazolium chloride (MEIC)} \) melts at various melt...
compositions. The Ga(III), added as GaCl₃ to the AlCl₃:MEIC melts, exhibited behavior similar to that obtained when added to AlCl₃: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 AlCl₃:MEIC melts, at approximately +1.3 V vs. Al (1:5:1) reference (Figure 4) is sharper than the oxidation peak in the corresponding AlCl₃: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. The consequence of slow electron transfer kinetics has meant that a large excess of gallium species over arsenic species is required to obtain codeposited films of GaAs. For this reason, we have recently commenced a study of chlorogallate melts from which, it is hoped, more favorable electron transfer kinetics can be achieved (11).

Aluminum Underpotential Deposition

A second reason to use chlorogallate media would be to reduce the possibility of unwanted Al codeposition, possibly as AlAs, in GaAs films. Deposition of metals at potentials more positive than their thermodynamic reversible potentials 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, Eₓ, may be expressed by

\[ Eₓ > Eₒ + \frac{RT}{zF} \ln \frac{aM^{2+}}{aM} \]

In this expression, Eₒ 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), Ti(I) and Cu(II), e.g. (12), on Au. In addition, this same phenomenon is well known with regards to the formation of monolayers of atomic hydrogen on Ir, Pt and Rh electrodes (13). Similar behavior occurs in molten salt systems. For example, using a LiCl-KCl molten salt systems, Schmidt investigated the deposition of Ag(I), Cd(II), Ni(II) and Pb(II) ions and briefly addressed monolayer formation processes (14). Hills et al. have studied the deposition of Ag and Ni on Pt from the LiCl-KCl eutectic at 400°C (15) and 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 indicate the presence of the UPD phenomenon. Figure 5 contains a voltammogram of Ga(III) at a slow scan rate (5 mV/s) in a very acidic, AlCl₃:BPC melt. After the second reduction wave, Ga(I) → 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 150 mV 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 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 (16). It is difficult to state if a GaAl intermetallic compound is responsible for this effect. This appears to be the first reported case for aluminum underpotential deposition.

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Table I. 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.

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

$^a$) Excess chloride ion fraction less the amount complexed with Ga(I).

Table II. Potentials and Ion Mole Fractions for Titration of $5.93 \times 10^{-2}$ M Ga(I) in a 1.25:1 AlCl$_3$:BPC Melt at 40°C.

| E, V | Ga(I)     | Cl$^-$ in excess to 1:1 | GaCl$_2^-$ | Cl$^-$$^a$ |
|------|-----------|-------------------------|------------|------------|
| -0.920 | 2.57 x 10$^{-21}$ | 1.02 x 10$^{-2}$ | 6.01 x 10$^{-3}$ | 6.16 x 10$^{-3}$ |
| -0.983 | 2.32 x 10$^{-22}$ | 2.94 x 10$^{-2}$ | 5.94 x 10$^{-3}$ | 1.75 x 10$^{-2}$ |
| -1.002 | 1.15 x 10$^{-22}$ | 4.53 x 10$^{-2}$ | 5.88 x 10$^{-3}$ | 3.33 x 10$^{-2}$ |
| -1.021 | 5.69 x 10$^{-23}$ | 6.54 x 10$^{-2}$ | 5.72 x 10$^{-3}$ | 5.39 x 10$^{-2}$ |
| -1.037 | 3.069 x 10$^{-23}$ | 8.90 x 10$^{-2}$ | 5.58 x 10$^{-3}$ | 7.78 x 10$^{-2}$ |
| -1.054 | 1.65 x 10$^{-23}$ | 1.06 x 10$^{-1}$ | 5.47 x 10$^{-3}$ | 9.52 x 10$^{-2}$ |

$^a$) Excess chloride ion fraction less the amount complexed with Ga(I).
Figure 1. Nernst plot of Ga(I)/Ga(0) vs. Al(2:1) ref. for a 1.5:1 AlCl₃:BPC melt, 35°C.

Figure 2. Potentiometric titration of Ga(I) as a function of AlCl₃:BPC melt acidity, 35°C.
Figure 3. Variation of the cell potential with the calculated chloride ion mole fraction in basic AlCl$_3$:BPC.

(A) 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.

Figure 4. CV of ~30 mM Ga(III) at 50 mV/s, W electrode area 7.06 mm$^2$, in (1.1:1) AlCl$_3$:MEIC, 25°C.
Figure 5. CV of ~15 mM Ga(III) at 5 mV/s, Pt button area 0.810 mm$^2$, in (1.87:1) AlCl$_3$:BPC, 40°C.