Electrodeposition of Bi$_{1-x}$Sb$_x$ Thin Films

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Bismuth and antimony are semimetals with unusual thermal, electrical, and magnetic transport properties. Both elements have a rhombohedral crystal structure with similar lattice parameters and form a solid solution over the entire composition range. Interest in these elements is largely due to their small carrier effective masses and hence high mobilities. Bismuth exhibits very low carrier concentrations and long carrier mean free paths leading to a very large magnetoresistance effect in bulk single crystals or thin films. Bismuth and antimony alloys are semimetals over most of the compositional range but are semiconductors for 0.07 $\leq x \leq 0.22$, with a maximum band gap of about 30 meV at about 1.43 cm$^{-2}$. The area of the film was 1.43 cm$^2$. After deposition, the films were thoroughly rinsed with 1 M HCl, rinsed with distilled DI water, and finally dried in a nitrogen flow.

X-ray diffraction (XRD) measurements were performed on a Philips X’pert X-ray diffractometer using a Cu Kα source. All scans were performed with a step width of 0.01° and at a scan rate of 0.02° s$^{-1}$. The instrument was calibrated before each measurement using the Si(004) peak. The composition of the deposited films was determined from wavelength dispersive X-ray spectroscopy (WDS) using a Jeol 8600 Superprobe. Compositions were obtained using a 20 μm diam beam taking the average of ten measurements at different locations on the film.

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Electrochemical measurements were performed under ambient conditions in a three-electrode cell with a platinum counter electrode and a Ag/AgCl (3M NaCl(aq)) reference electrode [U$_{eq}$ = 0.215 V (saturated hydrogen electrode, SHE)] positioned close to the working electrode using a Luggin capillary. The working electrode was a 200 nm thick polycrystalline gold film evaporated onto a Si(100) wafer with a 15 nm Cr adhesion layer. The electrode area was 0.2 cm$^2$. Electrical contact to the gold films was made with colloidal silver paste (Electron Microscopy Sciences). The solution used for deposition of Bi$_{1-x}$Sb$_x$ alloys was an aqueous solution of (0.1 $\leq x \leq 0.22$) M BiCl$_3$ + y M SbCl$_3$ + 2.4 M HCl + 0.03 M ethylenediaminetetraacetic acid (EDTA) with the SbCl$_3$ concentration, y, ranging between 0 and 0.1 M. Prior to each experiment the Au surface was etched with 10 vol % HNO$_3$ for 30 s, rinsed with distilled, deionized (DI) water, rinsed with 2.4 M HCl, and finally rinsed with the (0.1 $\leq x \leq 0.22$) M BiCl$_3$ + y M SbCl$_3$ solution.

The deposition efficiency was determined by depositing films at constant potential for 50 s and then stripping by scanning the potential to +0.4 V at a scan rate of 10 mV s$^{-1}$. The deposition efficiency was determined from the ratio of the stripping charge to the deposition charge for solutions with 0% Sb, 18% Sb, 70% Sb, and 100% Sb.

Bi$_{1-x}$Sb$_x$ films for physical characterization were electrodeposited at 7 mA cm$^{-2}$ for 200 s using a two-electrode arrangement. The substrate was a 100 nm thick gold film sputter deposited on a Si(100) wafer with a presputtered Cr adhesion layer. The deposition charge of 1.4 C cm$^{-2}$ corresponds to a film thickness of 1.0 μm for Bi and 0.88 μm for Sb, assuming 100% deposition efficiency. The composition of the deposited films was determined from wavelength dispersive X-ray spectroscopy (WDS) using a Jeol 8600 Superprobe. Compositions were obtained using a 20 μm diam beam taking the average of ten measurements at different locations on the film.

Experimental

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Speciation

Figure 1 shows the concentration of the relevant Bi(III) and Sb(III) chloride complexes vs. the mole fraction of Sb in solution for a total metal ion concentration [Bi(III) + Sb(III)] of 0.1 M. The solution composition was calculated from the stability constants $\beta_n$ for BiCl$_3$ and SbCl$_3$ summarized in Table I. The details are provided in the Appendix. The concentration of uncomplexed Bi$^{3+}$ and Sb$^{3+}$ ions is negligibly small; for a 0.1 M BiCl$_3$ solution, the Bi$^{3+}$ concentration is 1.60 $\times 10^{-10}$ M; for a 0.1 M SbCl$_3$ solution, the Sb$^{3+}$ concentration is 3.0 $\times 10^{-8}$ M. Figure 1b shows the percentage of each Bi(III) and Sb(III) complex with respect to the total Bi(III) or Sb(III) concentration vs. the mole fraction of Sb in solution. This figure illustrates that the hexachloride and pentachloride complexes are the dominant bismuth species in solution at about 60 and 40%, respectively. The pentachloride, hexachloride, and tetrachloride complexes are the main antimony species at 50, 25, and 20%, respectively. In all cases, the percentages are almost independent of the Sb/Bi ratio in solution.

For the case of antimony, even at low pH, the concentration of the antimony cation SbO$^-$ must also be considered.

\[
SbO^-(aq) + 2H^+(aq) + 3e^- \leftrightarrow Sb(s) + H_2O \tag{1}
\]

The formation of the oxyion from uncomplexed Sb$^{3+}$ ions and water is given by

\[
Sb^{3+}(aq) + H_2O \leftrightarrow SbO^-(aq) + 2H^+(aq) \tag{2}
\]
The equilibrium constant, \( K_{eq} \), for Reaction 2 can be determined from the standard potential for the \( \text{Sh}^{3+}/\text{Sh} \) redox couple \( U^{0}_{\text{Sh}^{3+}/\text{Sh}} = 0.26 \text{ V (SHE)} \) and the Nernst equation for Reaction 1 with \( U^{0}_{\text{SbO}^{3-}/\text{Sb}} = 0.204 \text{ V (SHE)} \):

\[
K_{eq} = \frac{[\text{SbO}^{3-}][\text{H}^+]^2}{[\text{Sh}^{3+}]} = 9.8 \times 10^2 \text{ mol}^2\text{L}^{-2}
\]

For an \( \text{H}^+ \) concentration of 2.4 M, the \( \text{SbO}^{3-} \) concentration is \( 1.8 \times 10^{-6} \text{ M} \) for a 0.1 M \( \text{ShCl}_3 \) solution. This concentration is negligibly small and can be neglected.

The standard potentials for the bismuth chloride and antimony chloride complexes, denoted as \( U^{0}_{\text{MCI}^{3-}/\text{M}} \) with \( \text{M} = \text{Bi} \) or \( \text{Sb} \), are related to the standard potentials of the uncomplexed \( \text{Bi}^{3+} \) and \( \text{Sb}^{3+} \) ions, \( U^{0}_{\text{M}^{3+}/\text{M}} \), through their respective stability constants \( \beta_n \) and at 298 K:

\[
U^{0}_{\text{MCI}^{3-}/\text{M}} = U^{0}_{\text{M}^{3+}/\text{M}} - \frac{RT}{3F} \log \beta_n = U^{0}_{\text{M}^{3+}/\text{M}} - 0.0197 \log \beta_n
\]

Reliable values of the standard potentials for the \( \text{Bi}^{3+}/\text{Bi} \) and \( \text{Sb}^{3+}/\text{Sb} \) couples are not known, since complexation and hydrolysis generally results in very small concentrations of uncomplexed \( \text{Bi}^{3+} \) and \( \text{Sb}^{3+} \) ions.\(^{19,22,23} \) As a result, the \( \text{Bi}^{3+}/\text{Bi} \) and \( \text{Sb}^{3+/Sb} \) redox potentials are obtained indirectly through measurements of their compounds and subsequent thermodynamic calculations.

For the \( \text{Bi}^{3+}/\text{Bi} \) equilibrium

\[
\text{Bi}^+ (aq) + 3e^- \leftrightarrow \text{Bi}(s)
\]

values of the standard potential reported in the literature are in the range 0.20 to 0.32 V (SHE).\(^{19,21,22,24} \)

For the \( \text{BiCl}_4^-/\text{Bi} \) equilibrium

\[
\text{BiCl}_4^- (aq) + 3e^- \leftrightarrow \text{Bi}(s) + 4\text{Cl}^- (aq)
\]

the standard potential \( U^{0}_{\text{BiCl}_4^-/\text{Bi}} \), calculated indirectly from the oxychloride compound, is 0.16 V (SHE).\(^{19,22,24} \) The standard potential for the \( \text{Bi}^{3+}/\text{Bi} \) couple calculated from the standard potential of the tetrachloride complex and its stability constant \( \beta_4 \) (see Table I) using Eq. 4 is \( U^{0}_{\text{Bi}^{3+}/\text{Bi}} = 0.28 \text{ V (SHE)} \).

For the \( \text{Sb}^{3+}/\text{Sb} \) equilibrium

\[
\text{Sb}^{3+} (aq) + 3e^- \leftrightarrow \text{Sb}(s)
\]

values for the standard potential are not available in the literature. For the antimony tetrachloride complex

\[
\text{SbCl}_4^- (aq) + 3e^- \leftrightarrow \text{Sb}(s) + 4\text{Cl}^- (aq)
\]

the standard potential \( U^{0}_{\text{SbCl}_4^-/\text{Sb}} = 0.17 \text{ V (SHE)} \).\(^{19,23} \) From the value for \( U^{0}_{\text{SbCl}_4^-/\text{Sb}} \) and the stability constant \( \beta_4 \) (see Table I), the standard potential for uncomplexed \( \text{Sb}^{3+} \) ions determined from Eq. 4 is \( U^{0}_{\text{Sb}^{3+}/\text{Sb}} = 0.26 \text{ V (SHE)} \).

The equilibrium potentials for bismuth and antimony for any solution composition can be determined either from the concentration of uncomplexed \( \text{M}^{3+} \) ions or from the concentration of the chloride complexes \( \text{MCI}^{3-}_n \) in solution using the Nernst equation. For the uncomplexed \( \text{M}^{3+} \) ions we obtain

\[
U_{eq} = U^{0}_{\text{M}^{3+}/\text{M}} + 0.0197 \log [\text{M}^{3+}]
\]

For the chloride complexes \( \text{MCI}^{3-}_n \) we obtain

\[
U_{eq} = U^{0}_{\text{MCI}^{3-}_n/\text{M}} + 0.0197 \log \left[ \frac{[\text{MCI}^{3-}_n]}{[\text{Cl}^-]^n} \right]
\]

The standard potentials for the different \( \text{BiCl}_4^{3-}_n \) and \( \text{SbCl}_4^{3-}_n \) species calculated from Eq. 4 are summarized in Table II. The stan-

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**Table I. Stability constants \( \beta_n = [\text{MCI}^{3-}_n]/[\text{M}^{3+}][\text{Cl}^-]^n \).**

<table>
<thead>
<tr>
<th>( \text{M} )</th>
<th>( \beta_1 )</th>
<th>( \beta_2 )</th>
<th>( \beta_3 )</th>
<th>( \beta_4 )</th>
<th>( \beta_5 )</th>
<th>( \beta_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>( 2.3 \times 10^2 )</td>
<td>( 3.1 \times 10^3 )</td>
<td>( 2.24 \times 10^5 )</td>
<td>( 1.26 \times 10^6 )</td>
<td>( 5.25 \times 10^6 )</td>
<td>( 3.63 \times 10^6 )</td>
</tr>
<tr>
<td>Sb</td>
<td>( 1.8 \times 10^2 )</td>
<td>( 3.1 \times 10^3 )</td>
<td>( 1.5 \times 10^4 )</td>
<td>( 5.3 \times 10^4 )</td>
<td>( 5.2 \times 10^4 )</td>
<td>( 1.3 \times 10^4 )</td>
</tr>
</tbody>
</table>
Table II. Standard potentials $U^{\circ}_{\text{MC}_{n}^{\pm} \rightarrow \text{M}}$ (V vs. SHE) for uncomplexed metal ions ($n = 0$) and metal chloride complexes (for $1 \leq n \leq 6$) determined from Eq. 4 and the stability constants given in Table I. MCl$_n^{3-n}$ + 3e$^-$ $\rightarrow$ M + nCl$^-$.

<table>
<thead>
<tr>
<th>n</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$U^{\circ}_{\text{BiCl}^{3+} \rightarrow \text{Bi}}$</td>
<td>0.28</td>
<td>0.23</td>
<td>0.21</td>
<td>0.17</td>
<td>0.16</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>$U^{\circ}_{\text{SbCl}^{3+} \rightarrow \text{Sb}}$</td>
<td>0.26</td>
<td>0.22</td>
<td>0.19</td>
<td>0.19</td>
<td>0.17</td>
<td>0.17</td>
<td>0.18</td>
</tr>
</tbody>
</table>

standard potentials for the chloride complexes of both elements with $n > 2$ are very close indicating that bismuth and antimony will codeposit as an alloy even at low overpotentials.

In summary, well defined values for $U^{\circ}_{\text{M}^{1+} \rightarrow \text{M}}$ and $U^{\circ}_{\text{MCl}_{2}^{3+} \rightarrow \text{M}}$ are not available. In the literature, the standard potentials for the tetrachloro complexes are $U^{\circ}_{\text{BiCl}_{4}^{3+} \rightarrow \text{Bi}} = 0.16$ V (SHE) (determined indirectly) and $U^{\circ}_{\text{SbCl}_{4}^{3+} \rightarrow \text{Sb}} = 0.17$ V (SHE). The standard potentials for the Bi$^{3+}$/Bi and Sb$^{3+}$/Sb couples obtained from the tetrachloro complexes using the relevant stability constants are $U^{\circ}_{\text{BiCl}_{4}^{3+} \rightarrow \text{Bi}} = 0.28$ V (SHE) and $U^{\circ}_{\text{SbCl}_{4}^{3+} \rightarrow \text{Sb}} = 0.26$ V (SHE).

Results and Discussion

Figure 2 shows current-potential curves for gold in (0.1 - $y$) M BiCl$_3$ + $y$ M SbCl$_3$ + 2.4 M HCl + 0.03 M EDTA, with Sb(III) mole fractions from 0% ($y = 0$) to 100% ($y = 0.1$ M). All solutions exhibit characteristic bulk deposition and stripping peaks. The separation between the peaks increases with increasing Sb(III) concentration in solution indicating that deposition and stripping become more irreversible with increasing Sb(III) concentration. The decrease in the peak current density with increasing Sb(III) concentration is also indicative of increasing irreversibility. Underpotential deposition was observed between the open-circuit potential (OCP) (+0.5 V vs. Ag/AgCl) and -0.1 V for all solutions, but is not considered further here.

The equilibrium potentials for the Bi(III)/Bi and Sb(III)/Sb couples can be experimentally identified from the potential of zero current in the reverse scan. The standard potentials can subsequently be determined using Eq. 9 and 10. Figure 3 shows the potential of

Figure 2. Current/voltage curves for (0.1 - $y$) M BiCl$_3$ + $y$ M SbCl$_3$ + 2.4 M HCl + 0.03 M EDTA, with Sb(III) mole fractions from 0% ($y = 0$) to 100% ($y = 0.1$ M). The mole percent of Sb(III) in the solution is indicated in the figure. The scan rate was 10 mV s$^{-1}$.

![Figure 2](image1.png)

Figure 3. (O) Zero-current potential, $U_{\text{OCP}}$, obtained from the reverse scan in current/voltage curves for solutions with (0.1 - $y$) M BiCl$_3$ + $y$ M SbCl$_3$ with $y$ varying from 0 to 0.1 M. The dashed lines show the equilibrium potentials for the Bi(III)/Bi and Sb(III)/Sb couples vs. the mole percent of Sb(III) in solution calculated (a) from the experimental equilibrium potentials for the pure components ($U_{\text{eq,Bi}} = -0.16$ V; $U_{\text{eq,Sb}} = -0.12$ V) and (b) from the partial standard equilibrium potentials $U^{\circ}_{\text{Bi}} = U^{\circ}_{\text{Sb}} = 0.045$ V (Ag/AgCl) determined from a best fit of $U_{\text{mix}}$ for the mixed solutions to $U^{\circ}_{\text{mix}}$. The solid line corresponds to the mixed potential, $U_{\text{mix}}$, for the two component mixed solution calculated assuming a rule of mixtures for the pure components in a and b.

![Figure 3](image2.png)
zero current in the reverse scan, \(U_{i=0}\), obtained from solutions with \((0.1 - y) \text{ M } \text{BiCl}_3 + y \text{ M } \text{SbCl}_3\).

In 0.1 M BiCl\(_3\) solution, \(U_{i=0,\text{Bi}} = -0.16 \text{ V vs. Ag/AgCl}\) \((U_{\text{eq,Bi}} = 0.055 \text{ V vs. SHE})\). For the 0.1 M SbCl\(_3\) solution, \(U_{i=0,\text{Sb}} = -0.12 \text{ V vs. Ag/AgCl}\) \((U_{\text{eq,Sb}} = 0.095 \text{ V vs. SHE})\). From Eq. 9 it follows that \(U_{\text{bi}^{3+}/\text{Bi}}^\circ = 0.25 \text{ V (SHE)}\) and \(U_{\text{Sb}^{3+}/\text{Sb}}^\circ = 0.24 \text{ V (SHE)}\), close to the literature values obtained from the tetrachloride complexes.

The equilibrium potentials for the Bi(III)/Bi and Sb(III)/Sb couples in mixed solutions \((U_{\text{eq,Bi}}\) and \(U_{\text{eq,Sb}}\)) can now be calculated for all solution compositions from the values of \(U_{\text{eq,Bi}}^\circ\) and \(U_{\text{eq,Sb}}^\circ\) using Eq. 9 and the speciation data. The dependencies of \(U_{\text{eq,Bi}}\) and \(U_{\text{eq,Sb}}\) on Sb(III) concentration in solution, calculated from the standard potentials for pure Bi and Sb solutions, are shown in Fig. 3a. For a simple rule of mixtures, the equilibrium potential for the two component system is given by

\[
U_{\text{mix}} = (1 - x)U_{\text{eq,Bi}}^\circ + xU_{\text{eq,Sb}}^\circ
\]

where \(0 < x < 1\). The variation of \(U_{\text{mix}}\) with solution composition is also shown in Fig. 3a. It can be seen that there is about a 20 mV difference between the experimentally measured potentials for the mixed solutions \((U_{i=0,\text{mix}})\) and \(U_{\text{mix}}\) calculated from the zero current potentials for the pure solutions. However, fitting the experimental \(U_{i=0}\) values for the mixed solutions to \(U_{\text{mix}}\) by adjusting the equilibrium potentials for Bi and Sb \((U_{\text{eq,Bi}}\) and \(U_{\text{eq,Sb}}\)) resulted in a good correlation between \(U_{i=0}\) and \(U_{\text{mix}}\), as demonstrated in Fig. 3b. The fit shown in Fig. 3b was obtained for

\[
U_{\text{Bi}}^\circ = U_{\text{Sb}}^\circ = U_{\text{Bi}^{3+}/\text{Bi}_{1-x}\text{Sb}_x}^\circ = 0.26 \text{ V(SHE)}
\]

where \(U_{\text{Bi}_{1-x}\text{Sb}_x}^\circ\) is the standard potential for the alloy. The origin of the approximately 20 mV difference between the equilibrium potentials for the mixed solutions and the equilibrium potentials for the pure solutions is not known. Substitution of the equilibrium potentials into Eq. 11 using the Nernst equation then yields an expression for the equilibrium potential of the Bi\(_{1-x}\)Sb\(_x\) alloy. At 298 K

\[
U_{\text{Bi}_{1-x}\text{Sb}_x} = U_{\text{Bi}_{1-x}\text{Sb}_x}^\circ + \frac{0.0592}{3} \log([\text{Bi}^{3+}]^{1-x}([\text{Sb}^{3+}]^x))
\]

Equation 13 represents the Nernst equation for the electrochemical formation of a \(\text{Bi}_{1-x}\text{Sb}_x\) alloy from uncomplexed Bi\(^{3+}\) and Sb\(^{3+}\) ions

\[(1 - x)\text{Bi}^{3+} + x\text{Sb}^{3+} \leftrightarrow \text{Bi}_{1-x}\text{Sb}_x\]

When the scan direction was reversed at a potential slightly positive to the onset of the bulk deposition peak, a distinct stripping peak was observed in the reverse scan, indicating that prepeaks \(P_a\) and \(P_b\) are associated with deposition. The area under the prepeaks was in the range 0.5-1 mC cm\(^{-2}\), close to the values for a close-packed (001) monolayer of Bi (0.54 mC cm\(^{-2}\)) and Sb (0.60 mC cm\(^{-2}\)).
The separation between the bulk deposition peak and the stripping peak is about 90 mV for the 0.1 M BiCl₃ solution and 250 mV for the 0.1 M SbCl₃ solution. This illustrates the higher reversibility of the bismuth deposition/stripping reaction and the lower reversibility of the antimony deposition/stripping reaction. The bulk deposition and stripping peaks are almost independent of potential for Sb⁻³ concentrations < 30%, showing that the higher reversibility of the bismuth deposition/stripping reaction is maintained up to about 30% Sb⁻³. For solution compositions >30% Sb⁻³, the peak separation between the main reduction peak and the stripping peak becomes larger with increasing Sb⁻³ concentration due to the lower reversibility of the deposition/stripping reaction.

Figure 6 shows the scan rate dependence of the potentials associated with the bulk deposition peak, the prepeaks, and the stripping peak for 0.1 M BiCl₃ [0% Sb(III)], 0.05 M BiCl₃ + 0.05 M SbCl₃ [50% Sb(III)], and 0.1 M SbCl₃ [100% Sb(III)]. The increasing reversibility of the metal ion couples with decreasing Sb(III) concentration are again clearly seen. Accordingly, the scan rate dependence of the bulk deposition peak decreased from 30 mV/decade for 100% Sb(III) to 20 mV/decade for 50% Sb(III) to 10 mV/decade for 0% Sb(III).

Figure 7 shows the scan rate dependence of the current density associated with the bulk deposition peak, the prepeaks, and the stripping peak, as shown in Fig. 7b, consistent with monolayer formation either by random adsorption or by irreversible two-dimensional (2D) nucleation and growth.$$
The scan rate dependence of the current density for prepeak \( P_\beta \), associated with Bi deposition, exhibited an exponent of 0.7, i.e., between \( n^{0.5} \) and \( n^{1.0} \), as shown in Fig. 7c. Such behavior is consistent with models for reversible monolayer formation by 2D nucleation and growth.\(^{25}\) The peak current density \( i_p \) and peak potential \( U_p \) for this process are given by

\[
i_p = \frac{0.368}{a} K^2 q_m \nu
\]

\[ U_p = U_a^o + \frac{a}{K} \]  \[ \text{[15]} \]

where \( q_m \) is the charge associated with monolayer deposition, \( \nu \) is the scan rate, \( U_a^o \) is the equilibrium potential for adsorption, and \( a \) is constant associated with nucleation.\(^{25}\) The constant \( K \) is given by

\[
K = -9.04 + 2.303 \log \left[ \frac{N_0}{N_T} \left( \frac{k_n^0 k_s^2}{n^2 a^2 \nu} \right) \right] \]  \[ \text{[16]} \]

where \( N_0 \) is the number of active sites, \( N_T \) the total number sites per unit area, \( k_n^0 \) is the standard rate constant for nucleation, and \( k_s^2 \) is the standard rate constant for growth. Since \( K \) is dependent on scan rate, the peak potential and peak currents are also dependent on scan rate. Substitution of \( K \) from Eq. 16 into Eq. 15 gives

\[
i_p (U_p - U_a^o)^2 = 0.368 a q_m \nu \]  \[ \text{[18]} \]

For a reversible process, the standard adsorption potential can be approximated by the onset potential for deposition. Figure 7c shows the scan rate dependence of \( i_p (U_p - U_a^o)^2 \) for prepeak \( P_\beta \), substituting the onset potential for the adsorption potential. The linear dependence of \( i_p (U_p - U_a^o)^2 \) on scan rate is consistent with Eq. 18. The slope in Fig. 7c corresponds to 0.368 \( a q_m \). The parameter \( a \) can be obtained from the dependence of the peak potential on scan rate. Combining Eq. 16 and 17 we obtain

\[
(U_p - U_a^o)^{-1} = \frac{9.04}{a} + \frac{2.303}{a} \log \left[ \frac{N_0 k_n^0 k_s^2}{n^2 a^2 \nu} \right] + \frac{6.91}{a} \log \nu \]  \[ \text{[19]} \]

\(^{25}\) \( a = -\pi^2 r^2 \sigma \epsilon / k T \), where \( r \) is the island radius, \( \sigma \) is the energy per unit area, \( n \) is the number of electrons, \( \epsilon \) is the charge on the electron, \( k \) is the Boltzmann constant, and \( T \) is temperature.\(^{25}\)
Figure 11. Crystal structure of Bi and Sb. (a) Two rhombohedral unit cells on hexagonal axes. For Bi: $a = 0.474$ nm, $\alpha = 57.233^\circ$. (b) The hexagonal primitive cell has atoms on the corners of the parallelepiped as well as atoms at the $(2/3,1/3,1/3)$ and $(1/3,2/3,2/3)$ positions. For Bi: $a = b = 0.455$ nm, $c = 1.186$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$; for Sb: $a = b = 0.431$ nm, $c = 1.127$ nm, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The $(012)$ plane is also shown. (c) Normal view to the $(012)$ plane, illustrating the two-fold symmetry in this plane.

Figure 12. The lattice spacing in the $(012)$ direction determined from the diffraction peak vs. the Sb concentration in the film.

Figure 13. Scanning electron microscope plan view images for Bi$_{95}$Sb$_5$, Bi$_{70}$Sb$_{30}$, and Bi$_{10}$Sb$_{90}$ films.

Figure 14. Cross-sectional scanning electron microscope image of a Bi$_{95}$Sb$_5$ film illustrating a characteristic columnar microstructure.
Thin film characterization.—Figure 9 shows the mole fraction of Sb in films deposited at 7 mA cm$^{-2}$ vs. the mole fraction of Sb(III) in solution. The Sb concentration in the film is slightly lower than predicted by the linear dependence at low Sb(III) concentrations in solution (<30% Sb(III)) and slightly higher at larger Sb(III) concentrations in solution. The crossover at 30% Sb(III) corresponds to the limit of Bi-dominated reversible deposition and stripping (<30% Sb(III)). At higher concentrations of Sb(III), the deposition reaction is dominated by the more irreversible Sb deposition/stripping reaction.

Bismuth and antimony form a rhombohedral crystal structure. For convenience, however, the crystal structures are usually represented on hexagonal axes, with a trigonal $c$ axis along the [001] direction and the twofold or binary $a$ and $b$ axes normal to the trigonal direction and 120° apart from each other. The Bi$_{1-x}$Sb$_x$ planes are also shown in Fig. 11b. Figure 11c shows a normal view to the (2/3,1/3,1/3) and (1/3,2/3,2/3) positions. The 2D unit cells for the hexagonal close-packed (001) planes of Bi and Sb are diamond shaped with sides of 0.4546 and 0.4308 nm, respectively. The close-packed (001) planes are arranged in bilayers along the [001] direction so that crystals are easily cleaved perpendicular to the trigonal axis. As described previously, the deposition of a close-packed (001) monolayer corresponds to 0.54 mC cm$^{-2}$ for Bi and 0.60 mC cm$^{-2}$ for Sb. The (012) plane is also shown in Fig. 11b. Figure 11c shows a normal view to the (012) plane, illustrating the two-fold symmetry in this plane, with two layers of atoms one slightly above and one slightly below the plane. The deposition of an (012) monolayer corresponds to 0.45 mC cm$^{-2}$ for Bi and 0.50 mC cm$^{-2}$ for Sb.

Figure 12 shows the lattice spacing in the (012) direction determined from the diffraction peak. This figure illustrates that the lattice spacing increases monotonically from Sb to Bi according to Vegard’s rule, consistent with the formation of a homogeneous solid solution. Similar results have been reported for Bi$_{1-x}$Sb$_x$ films deposited at constant current.

For all compositions the films were matte gray and exhibited facets of grains ranging from about 1 μm in size for pure Bi to several micrometers for pure Sb films. Figure 13 shows scanning electron microscope plan view images for Bi$_8$Sb$_{50}$, Bi$_9$Sb$_{49}$, and Bi$_9$Sb$_{30}$ films. These images illustrate the progressive increase in grain size with increasing Sb content. These results are consistent with the faster kinetics for bismuth deposition reaction which would be expected to lead to higher cluster density and hence smaller grain size. Figure 14 shows a cross-sectional image of a Bi$_{30}$Sb$_{70}$ film illustrating a characteristic columnar microstructure.

Conclusions

Homogeneous Bi$_{1-x}$Sb$_x$ alloys can be electrodeposited from acidic chloride-based solutions. Bulk deposition is preceded by monolayer deposition at potentials negative to the equilibrium potential. The deposition/stripping reaction for bismuth is more reversible than for antimony leading to a small increase in the bismuth concentration in films compared to the concentration in solution at low Sb(III) concentrations. Thin films have a preferred (012) texture and the interplanar spacing is proportional to the film composition according to Vegard’s rule. The grain size for thin films increases from about 1 μm for pure Bi to several micrometers for pure Sb.

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Appendix

For the determination of speciation, the following species were considered: Bi$^{3+}$, BiCl$^+$, SbCl$^+$, SbCl$_2^+$, SbCl$_3^+$, SbCl$_4^-$, and Cl$^-$. The species BiCl$^+ _2$, BiCl$_3^+$, SbCl$_4^-$, and SbCl$_6^-$ were not considered since their stability constants are negligible.

The stability constants for bismuth and antimony are given by

$$\beta_{s} = \frac{[\text{BiCl}^+]}{[\text{Bi}^+] [\text{Cl}^-]} \quad [A1]$$

$$\beta_{s} = \frac{[\text{SbCl}^-]}{[\text{Sb}^+] [\text{Cl}^-]} \quad [A2]$$

The values for the relevant stability constants are given in Table I. In addition to the equilibria for the bismuth and antimony species we have five mass balance equations

$$3\text{c}_{\text{BiCl}_3} + \text{c}_{\text{HCl}} + 3\text{c}_{\text{SbCl}_3} = [\text{Cl}^-] + 4[\text{BiCl}^+] + 5[\text{SbCl}^+] + 6[\text{SbCl}_2^-]$$

$$+ 3[\text{SbCl}_3] + 4[\text{SbCl}_4^-] + 5[\text{SbCl}_6^-] + 6[\text{SbCl}_7^-] \quad [A3]$$

$$\text{c}_{\text{BiCl}_3} = [\text{BiCl}^+] + [\text{BiCl}_3^+] + [\text{BiCl}_4^-] = [\text{Bi}^{3+}][\text{Cl}^-]^4 + \beta [\text{Cl}^-] [\text{Cl}^-]^3$$

$$+ \beta^{3*} [\text{Cl}^-]^{-3} \quad [A4]$$

$$\text{c}_{\text{SbCl}_3} = [\text{SbCl}^-] + [\text{SbCl}_2^-] + [\text{SbCl}_3^-] + [\text{SbCl}_4^-] = [\text{Sb}^{3+}][\text{Cl}^-]^3$$

$$\quad + \beta [\text{Cl}^-] [\text{Cl}^-] + \beta^{3*} [\text{Cl}^-]^3 \quad [A5]$$

$$\text{c}_{\text{BiCl}_3} + \text{c}_{\text{SbCl}_3} = 0.1 \text{ M} \quad [A6]$$

$$\text{c}_{\text{HCl}} = 2.4 \text{ M} \quad [A7]$$

Substitution of A-4, A-5, A-6, and A-7 into A-3 gives the relationship between the chloride ion concentration in solution, [Cl$^-$], and the total concentration of bismuth chloride, [c$_{\text{BiCl}_3}$], and antimony chloride, [c$_{\text{SbCl}_3}$], added to the solution

$$(\text{[Cl}^-] - 2.71) + (0.1 - c_{\text{SbCl}_3}) \left[ 4[\text{BiCl}^-][\text{Cl}^-] + 5[\beta [\text{Cl}^-] [\text{Cl}^-] + 6[\beta^{3*} [\text{Cl}^-]^{-3}$$

$$\quad + \beta [\text{Cl}^-] [\text{Cl}^-] + \beta^{3*} [\text{Cl}^-]^3 \right]$$

$$\quad + \beta [\text{Cl}^-] [\text{Cl}^-] + \beta^{3*} [\text{Cl}^-]^3 + \beta [\text{Cl}^-] [\text{Cl}^-]$$

$$\quad + \beta^{3*} [\text{Cl}^-]^3 \right] = 0 \quad [A8]$$

For each solution composition (c$_{\text{SbCl}_3}$) the chloride concentration ([Cl$^-$]) was determined from the zero intercept of Eq. A-8 with chloride concentration ([Cl$^-$]). Subsequently, the concentrations of free bismuth ions ([Bi$^{3+}$]) and free antimony ions ([Sb$^{3+}$]) were calculated from Eq. 4 and 5. The concentration of each bismuth and antimony chloride complex, BiCl$_{3n}$ and SbCl$_{3n}$, was then calculated from the relevant stability constant $\beta_{s}$.  

References


