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Electrodeposition of SbTe thin films was investigated at room temperature, where amorphous deposits were obtained. The electrodeposition of Sb was found to be induced by Te, while the latter was not affected by the Sb. Detailed studies on this induced deposition were carried out by varying the Sb(III) and Te(IV) concentrations, pH, and agitation. The Sb deposition rate was found to be independent of the concentrations of both species but dependent on the pH and agitation. A phase transition from amorphous films into crystalline Sb₂Te₃ at 120°C was observed for the plated SbTe. (© 2007 The Electrochemical Society. [DOI: 10.1149/1.2806169] All rights reserved.

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Electrodeposition of compound semiconductor materials, including II–VI,¹ III-V,²⁻⁴ III-VI,⁵ IV-VI,⁶ and V-VI ⁷⁻¹¹ binary compounds and some ternary compounds,¹² have been attracting more and more attention as they find many applications in optical, photovoltaic, phase-change solid memory, and thermoelectronic devices. Among them, SbTe can be used, either alone or by alloying with other elements, for solar cells,¹³ thermoelectric devices,¹⁴ and phase-change devices.¹⁵

Phase-change devices use materials that can be switched between two distinct states, amorphous and crystalline. Some properties of the materials are so different at these two states that they can be used as digital information for microelectronic applications such as rewritable optical storage and solid-state memory. Sb-based alloys, particularly SbTe-based alloys, are currently being studied extensively as phase-change materials.¹⁵ However, these phase-change studies are all based on materials deposited by vacuum processes.

Some limited studies have been recently reported on other processes,¹⁶⁻¹⁸ including electroplating,⁷⁻⁹ for the preparation of highly crystalline Sb_2Te_3 thin films and nanostructures. For example, Leimkühler et al.⁷ developed an electroplating process at relatively high temperature (~100°C) and successfully plated Sb₂Te₃ crystals. The deposit composition could be adjusted by the Sb/Te ratio in the plating solution and the lattice parameter was found to change gradually from Sb to Sb₂Te₃. Furthermore, by using an electrochemical atomic layer deposition (ECALD) process, Yang et al.⁹ electroplated highly crystalline Sb₂Te₃ compounds on Pt substrate. Aside from these limited studies on the electrodeposition of crystalline SbTe, no studies have been reported on the amorphous SbTe alloys, which is of great interest for phase-change applications. In this report, electrodeposition was carried out at room temperature, where amorphous SbTe alloys are obtained. Studies were focused on the interaction between the two elements during electrodeposition and an induced electrodeposition was reported. The phase-change property of the electrodeposited alloy was also characterized and reported for the first time.

Experimental

Electrodeposition was carried out at room temperature $(20^{\circ}C)$ in solutions containing 0.21 M sodium citrate, 1 M HNO₃, and various amounts of SbCl₃ and TeO₂. The details of the solution ingredients are listed in Table I. In order to make the alloy solution, SbCl₃ and TeO₂ were dissolved separately in sodium citrate solution and concentrated HNO₃, respectively, and were then mixed under agitation. The pH of the final solution was adjusted with NaOH. At the pH of this study, the Sb and Te were expected to be present in the forms of SbO⁺ and HTeO₂⁺, respectively.^{7,12,19} However, due to the presence of the citrate complexing agent, Sb(III) and Te(IV) are used in this paper to refer to the cation species in solution.

A traditional three-electrode cell was used for electrodeposition.

A platinum mesh was used as counter electrode and a saturated calomel electrode (SCE) as reference. The working electrode is a rotating disk electrode (RDE), onto which a cathode substrate was mounted. Cu plates and Si covered by a physical vapor deposited (PVD) TiN layer were used as cathodes for polarization studies and galvanostatic plating, respectively. In order to avoid the ohmic error in potentiostatic plating due to the solution resistance and substrate resistance, partial current densities were obtained from the deposition rate of each element in galvanostatic plating experiments and the corresponding potential in the polarization studies. Except for cases otherwise stated in the report, the galvanostatic plating experiments were controlled by a constant total charge of 240 mC/cm², corresponding to a film thickness of around 100-150 nm depending on the current efficiency. The transient effects due to the substrate characteristics and the nonsteady-state plating are believed to be minimized for a film within this thickness range.

Cu substrate was used in polarization studies to avoid any resistance of the substrates. The Cu plates were mechanically polished and cleaned with 0.5 M sulfuric acid before electroplating. Before each polarization study, the Cu substrate was preplated in the same solutions at -2 mA/cm^2 for 10 s to form a layer of Te or Te-rich layer. The Si wafers were antimony-doped n-Si(100) with a resistivity $<0.03 \ \Omega$ cm, cleaned by a standard RCA clean process to remove organic contamination and surface oxide. A layer of 75 nm TiN was deposited on Si by PVD, called TiN substrate in this paper. TiN substrates were used in all the galvanostatic plating experiments on which smoother deposits were achieved (see Results and Discussion section). A 1:100 dilute HF dip for 2 min followed by 18 $M\Omega$ deionized (DI) water rinse and nitrogen blow dry was carried out immediately before the Si or TiN was mounted onto the rotating disk electrode (RDE) for electrodeposition. InGa eutectic was used to ensure ohmic contact.

An EG&G 273 potentiostat by Princeton Applied Research, Inc., was used as a power source for the electrochemical studies. The morphology and crystal structure of the films were characterized with an AutoProbe atomic force microscope (AFM) under tapping mode and a Philips X-ray powder diffractometer with a Cu X-ray source ($K\alpha = 1.54$ Å). Time-resolved X-ray diffraction (XRD) was

Table I. Different solutions used in the study.

Solution	SbCl ₃ (mM)	TeO ₂ (mM)	Citrate (M)	HNO ₃ (M)	pH
1, Sb only	10		0.21	1	2.3
2, Te only		5.0	0.21	1	2.3
3	10	5.0	0.21	1	2.3
4	20	5.0	0.21	1	2.3
5	10	10.0	0.21	1	2.3
6	10	2.5	0.21	1	2.3
7	10	1.0	0.21	1	2.3
8	10	5.0	0.21	1	3.3

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Figure 1. Polarization curves in (i) Te-only and (ii) Sb-only solutions and (■) the partial current density of Sb deposition in the Sb-only solution.

performed at beamline X-20C of the National Synchrotron Light Source using an X-ray wavelength of 1.797 Å. The thickness of the pure elemental deposit was obtained with a KLA-Tencor stylus profilometer. The composition and thickness of the SbTe alloy films were obtained by proton-induced X-ray emission (PIXE) using protons at 1.15 MeV.²⁰ As the deposited films are extremely smooth on the TiN substrates, the thickness measurements are believed to be accurate enough for partial current density and current efficiency calculation.

Results and Discussion

Studies were first carried out in pure elemental plating solutions for Sb or Te (solutions 1 and 2 in Table I). Figure 1 shows the polarization curves in these two solutions. The pure Te plating current starts to increase at -0.3 V (SCE) and a current plateau was observed between -0.4 and -0.8 V (SCE). As the hydrogen evolution reaction on the Te surface has a very low overpotential and a high exchange current density,¹⁹ the current plateau observed in Te plating was believed to be the mass-transport control for the deposition of Te and the hydrogen evolution reaction. The plating current in the Sb solution starts to increase significantly at about -0.65 V (SCE). Galvanostatic plating was carried out at different current densities on TiN substrates, and the current efficiencies were calculated from the film thickness. As shown by the solid squares in Fig. 1, the current efficiency was close to 100% for pure Sb plating at low current density, consistent with the very low exchange current for hydrogen evolution reaction on Sb surface.¹⁹

At a pH of 2.3, the SbCl₃ and TeO₂ were believed to be present in forms of SbO⁺ and HTeO₂⁺¹⁹ According to Eq. 1 and 2, the reversible potentials are 0.17 and -0.16 V (SCE) for HTeO₂⁺ and SbO⁺, respectively. Because citrate was used in all solutions in this paper, deviation in the reversible potential is expected due to the complexing effect. However, Te deposition always started at a much more noble potential than Sb, as observed in Fig. 1

$$HTeO_2^+ + 3H^+ + 4e^- \rightarrow 2H_2O + Te$$

 $E^{0}(\text{NHE}) = 0.551 - 0.0443 \text{ pH} + 0.0148 \log(\text{HTeO}_{2}^{+})$ [1]

$$SbO^+ + 2H^+ + 3e^- \rightarrow H_2O + Sb$$

$$E^{0}(\text{NHE}) = 0.212 - 0.0394 \text{ pH} + 0.0197 \log(\text{SbO}^{+})$$
 [2]

Studies were then carried out in solution 3 in Table I, an alloy solution with the same concentrations as the elemental solutions but with both elements. Figure 2a shows the polarization curve with the partial current densities of Sb deposition, Te deposition, and the side reaction. The Te deposition was under mass-transport control for the



Figure 2. (a) The total current density (-) and partial current densities of (\blacksquare) Sb, (\blacktriangle) Te, (\times) side reaction, and (\bigcirc) the sum of Te and side reactions; and (b) the dependence of the deposit compositions, (\blacksquare) Sb, (\bigstar) Te, on the applied potential in a SbTe alloy solution containing 10 mM Sb and 5 mM Te.

potential range of study. The sum of the Te deposition and side reaction is the same as the total current in elemental Te plating presented in Fig. 1. In other words, the presence of Sb did not change the Te deposition. On the contrary, the Sb deposition was significantly altered by the codeposition of Te. The deposition potential of Sb was shifted to -0.4 V (SCE) as compared to -0.65 V in the case of elemental Sb deposition, a characteristic feature of induced electrodeposition. The following studies are mainly focused on this induced codeposition regime, or a potential range of -0.4 to -0.65 V (SCE).

Another observation to be noted in Fig. 2a is that the side reaction, mainly hydrogen evolution in the potential range of this study, decreased slightly as the Sb deposition rate increased. This is believed to be related to the different exchange current densities of the hydrogen evolution reaction on Te and Sb surfaces. This decrease of the side reaction rate has also been observed in all the alloy deposition studies in this report.

Figure 2b shows the composition of SbTe alloys plated at different potentials. Films were plated galvanostatically at different currents on TiN substrates. A total charge of 240 mC/cm² was used in the galvanostatic plating and the films were about 100–150 nm thick, depending on the current efficiencies. As expected from the different reversible potentials of the Te and Sb, the composition of the deposit strongly depended on the applied current or potential. The deposit is Te-rich at low potential, and the Sb content increases as the potential or current increases. Pure Te film was obtained at current densities lower than -3 mA/cm^2 . Films with up to 60 atom % Sb can be plated at -9 mA/cm^2 without delamination.



Figure 3. Comparison of the total current density (—) and partial current densities of (\blacksquare , \square) Sb and (\blacktriangle , \triangle) Te for two solutions with different SbCl₃ concentrations. The solutions have (i, \blacksquare , \bigstar) 5 mM TeO₂ and 10 mM SbCl₃; and (ii, \square , \triangle) 5 mM TeO₂ and 20 mM SbCl₃.

At an even higher current density, e.g., -10 mA/cm^2 , the films delaminate very easily, indicating a high stress in the films. Pure Sb film was never obtained from a mixed SbTe solution in the range of deposition parameters used in this study.

Figure 3 shows the effect of Sb(III) concentration in the solution on the partial current densities. Experiments were carried out in solution 4 in Table I, where the Sb(III) concentration is doubled from solution 3. Both the Te and Sb plating rates were not changed. While the noneffectiveness of Sb(III) concentration in changing the Te plating rate was consistent with the observations in Fig. 2, the unchanged Sb plating rate suggested that the Sb plating rate is completely dependent on the presence and the inducing effect of Te.

Detailed studies were further carried out on the effect of the Te(IV) concentration on the alloy deposition. Figure 4 presents the partial current densities and compositions of deposits from solutions with different Te(IV) concentrations. As expected, the Te plating rate increases with the Te(IV) concentration in the solutions. In the potential range of -0.4 to -0.65 V (SCE) the Sb plating rate is independent of the Te(IV) concentration for the range of study. It is evident from Fig. 2 and 3 that the Sb deposition at this potential range is induced by the presence of Te. If the induced codeposition results from a Te-comprising species in the solution and the amount of this species is dependent on the available Te(IV), an increase in the Te(IV) concentration would have increased the induction effect and thus increased the Sb deposition rate. However, the observation in Fig. 4b suggested this is not the case.

Figure 4c shows the dependence of alloy composition on the plating potential or current in different solutions. Films were plated on TiN substrates at galvanostatic mode up to a constant total charge, except for the films plated in low Te(IV) concentration solutions and at high current densities, where films delaminate easily. However, all the films were at least 40 nm thick to minimize the substrate effect in the transient region at the beginning of the plating. First, Te% increased with the Te(IV) concentrations at less negative potential. Second, as expected from the different reversible potentials for Sb and Te, the films are Te-rich at less negative potential and the Sb content increases as the potential becomes more negative. In addition, except for the films plated from 10 mM Te(IV), where much lower Sb content is always obtained, all the films reach a maximum Sb% of about 60 atom %. Further increase of the potential does not increase the Sb content in the film. As discussed above, this maximum Sb content may correspond to an upper limit for the induced deposition mechanism, above which elemental Sb is deposited and results in highly stressed films.

X-ray diffraction (XRD) was carried out to characterize both the elemental and alloy films. It was found that the as-plated pure Sb



Figure 4. Comparison of the total current density (—) and partial current densities of (a) Sb, (b) Te, and (c) deposit compositions, (—) Sb% and (- - -) Te%, for SbTe alloy solutions with 10 mM SbCl₃ and (\Box) 1 mM, (\diamond) 2.5 mM, (\blacksquare) 5 mM, and (\triangle) 10 mM TeO₂.

films were crystalline and the pure Te films were amorphous. Surprisingly, amorphous characteristics were observed for all the alloy films that were randomly picked for XRD analysis, with up to 50 atom % Sb. Therefore, the delamination of Sb-rich films may be related to the as-deposited crystalline Sb when elemental Sb starts to plate at high potentials. In addition, the fact that films with much higher Sb content could be plated at high temperature⁷ may suggest some differences in the nucleation and growth process at different temperatures.

Figure 5 shows the effect of agitation on the partial current densities and the deposit compositions. Studies were carried out in so-



Figure 5. Comparison of (a) total current density (—) and partial current densities of (\blacksquare , \square) Sb, and (\blacktriangle , \triangle) Te, and (b) deposit compositions, (—) Sb% and (- - -) Te%, for SbTe alloy solution at (i, \square , \triangle) 140 rpm and (ii, \blacksquare , \bigstar) 550 rpm.

lution 3 in Table I, the same as Fig. 2. The rotation rate of the disk electrode was decreased by a factor of four. As expected, the Te partial current density decreased with the agitation. However, the ratio of the Te plating current did not follow the square root of the rotation rate, suggesting that the Te deposition was under a mixed control by the reaction kinetics and the mass transport. At the same time, the Sb partial current density also decreased with the rotation rate. This observation is different from Fig. 3 and 4, where the Sb plating rate is independent from the Te(IV) or Sb(III) concentration in the solution. Because the main effect of changing the agitation rate is to change the mass-transport flux toward the electrode, the decrease of the Sb plating rate at a low agitation rate suggests species other than Sb(III) and Te(IV), such as H⁺, may play a role in the induced deposition of Sb.

Figure 5b presents the film compositions plated at different potentials with the two agitation conditions. Similar film compositions were observed for both conditions as the Te and Sb plating rates are both decreased at a low agitation. A plateau of up to 60 atom % Sb was still observed for the films due to a compositional limit where amorphous low-stress films can be obtained.

In order to further clarify the possible effect of H^+ in the deposition, the effect of solution pH was investigated. Figure 6 shows the partial current densities and film compositions of films plated from the solutions with two different pH values, 2.3 and 3.3. The electrodeposition started at a higher potential when a higher pH was used, as expected from the reversible potential change (Eq. 1 and 2).



Figure 6. Comparison of (a) total current density (—) and partial current densities of (\blacksquare , \square) Sb and (\blacktriangle , \triangle) Te, and (b) deposit compositions, (—) Sb% and (- - -) Te%, for SbTe alloy solutions with 10 mM SbCl₃ and 5 mM TeO₂ at pH (i, \square , \triangle) 3.3 and (ii, \blacksquare , \bigstar) 2.3.

In addition, an increase of pH from 2.3 to 3.3 is also expected to increase the complexing effect of citrate, which could also contribute to the shift of the plating potential.

Increasing pH decreases the Te plating rate in the less negative potential regime. This effect diminishes quickly as potential increases until a mass-transport-limited current density is reached. Furthermore, the Sb plating rate in the induced deposition regime is always decreased at a higher pH. Although the reaction listed in Eq. 2 is for the elemental Sb deposition, H^+ or pH is believed to play a critical role in the induced deposition of Sb as well.

Shown in Fig. 6b is the pH effect on the film composition plated at different potentials. An increase of pH decreases the Sb content and increases Te content, consistent with the observation in partial current densities, where the Sb plating rate was decreased at high pH while Te plating rate was less changed as the mass transport comes into play.

Induced electrodeposition has been observed in a number of alloy systems and different mechanisms have been proposed for the observations. For example, in the codeposition of CdTe, Cd is electrodeposited onto a Te-covered electrode surface through an underpotential deposition (UPD) process.²¹ However, the Sb deposition in this study does not change with the Te(IV) concentration, the Sb(III) concentration, or the Te coverage on the electrode, which would be expected for such a UPD process. A second mechanism^{22,23} that has been proposed for the induced

A second mechanism^{22,23} that has been proposed for the induced deposition of In in CuInSe alloys involves a chemical reaction. In this case, CuSe is first electrodeposited as a binary alloy. At a higher potential, the electrodeposited CuSe is further reduced into Cu₂Se



Figure 7. (Color online) AFM image showing the surface morphology of SbTe films: (a) 50 nm thick film on n-Si; (b) 150 nm thick film on n-Si; (c) 50 nm thick film on TiN; (d) 150 nm thick film on TiN. The root-mean-square roughness values for the four films are (a) 5.4, (b) 4.5, (c) 2.3, and (d) 2.2 nm.

and Se²⁻ anions. The resultant Se²⁻ anions are released into the solution and react with the In³⁺ cations, causing the formation of In₂Se₃ on the electrode surface. If the Sb deposition in this study was induced in the same fashion, the Sb deposition rate would have depended on the Te coverage on the electrode. In addition, the induced Sb deposition in this study started at a much less negative potential than the formation of Te²⁻, indicating that other mechanisms play a critical role.

A different approach to tackle the induced deposition mechanism involves hybrid intermediate species comprised of both elements in alloy systems. For example, a $[(Ni)(HWO_4)(Cit)]^{2-}$ complexed species in the bulk solution²⁴ and a $[(Ni)(MoO_2)(Cit)]^-$ adsorbed species on the electrode²⁵ have been proposed to explain the induced deposition of W and Mo in the NiW and NiMo systems, respectively. Both mechanisms suggest that the plating rate of the induced species depends on the concentrations of the complexing agent and both the inducing and the induced species.

In this study, the Sb deposition rate was found to be independent of Sb(III) and Te(IV) concentration but dependent on the pH and agitation. These observations may suggest a hybrid species comprised of H⁺ is involved in the Sb-induced deposition. Because the elemental deposition of Te and Sb both consume H⁺, the electrode surface pH is believed to be much different from the bulk pH. While an excessive amount of citrate was used in this study, the H⁺ flux toward the electrode surface seems to be the rate-determining factor for the induced deposition of Sb. Further studies are needed to confirm this intermediate species and to determine whether or not it is adsorbed on the electrode surface.

Figure 7 shows the surface morphology of the electroplated SbTe films characterized with AFM. The films were plated at the a constant current of -9 mA/cm^2 for different times, having a composition of 53–57 atom % Sb and 43–47 atom % Te. Two different substrates were used for comparison, TiN-covered and bare n-Si. No significant topographical feature was observed under top-down scanning electron microscopy (SEM) inspection for the four films shown in Fig. 7. At a magnification of 50 k, the top-down SEM micrographs correspond well to the AFM images. The AFM images were obtained on a $1 \times 1 \mu m$ area and the vertical scale is 30 nm/grid. It is evident that the film thickness has little impact on film size strongly depend on the substrate. The films plated on TiN have



Figure 8. (Color online) (a) Intensity of diffracted X-ray as a function of temperature for a heating rate of 1° C/s for a SbTe film plated on TiN; (b) θ -2 θ pattern for the same sample, (b1) before and (b2) after the temperature ramping process.

much smoother surface and finer grains than the ones on Si, suggesting different nucleation and growth behaviors on the two different substrates.

The crystallization transition behavior of the as-deposited amorphous films was also characterized for phase-change device applications. Figure 8a shows the intensity of diffracted X-ray as a function of sample temperature for a $Sb_{49}Te_{51}$ film plated on TiN. A linear detector was used to record the intensity of the diffracted X-ray simultaneously over a 20 range from 24 to 39°. The X-ray wavelength, $\lambda,$ was 1.797 Å and the sample temperature was ramped from 20 to over 400°C at a rate of 1°C/s in a purified helium atmosphere to avoid oxidation. Figure 8b shows the θ -2 θ spectra obtained for the same film before and after the temperature ramp using the same X-ray source with a 2θ range of $20-60^\circ$. Before the annealing, no crystalline diffraction was observed, except two small peaks from the TiN substrate, and a broad peak resulted from the amorphous SbTe film. The film was converted into crystalline states after the annealing. All the diffraction peaks can be ascribed to Sb₂Te₃ crystal. A transition from amorphous SbTe to crystalline Sb₂Te₃ phase was observed at 120°C, as shown in Fig. 8a. This low transition temperature reflects a low activation energy for crystallization and is consistent with the observation that crystalline Sb₂Te₃ could be obtained by electrodeposition at boiling temperature $(\sim 100^{\circ}\text{C})$.' Furthermore, it was expected from phase diagrams²⁶ that Sb₂Te₃ phase has a very small range of compositions, with Sb between 40 and 40.4%. However, the film shown in Fig. 8 has a much higher Sb%. In addition, three other SbTe films with Sb content ranging from 37 to 57 atom % were found to crystallize into the Sb₂Te₃ phase at similar temperatures. This wide range of composition suggests that some residue amorphous SbTe alloy or other crystalline phase, such as Sb, Sb-rich δ and γ phases, or Te phase, may be present after annealing. However, they were not observed in the θ -2 θ spectra in the presence of the crystalline Sb₂Te₃.

Conclusion

Electrodeposition of SbTe thin films was investigated in citrate baths at room temperature. Amorphous deposits were obtained as

plated, which crystallized into Sb₂Te₃ at 120°C. The substrate for the deposition was found to strongly impact the surface roughness and grain size. While an induced electrodeposition was observed for Sb in the alloy system, the deposition rate of Sb was found to be independent of the concentration of the Sb and Te for the range of study. Solution pH and agitation conditions were found to impact the Sb deposition rate, which may suggest that the rate-determining step for the deposition involves a proton-incorporated intermediate species.

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References

- 1. M. K. Mathe, S. M. Cox, B. H. Flowers, Jr., R. Vaidyanathan, L. Pham, N. Srisook,
- U. Happek, and J. L. Stickney, J. Cryst. Growth, 271, 55 (2004).
 T. L. Wade, R. Vaidyanathan, U. Happek, and J. L. Stickney, J. Electroanal. Chem., 500, 322 (2001).
- 3. T. Fulop, C. Bekele, U. Landau, J. Angus, and K. Kash, Thin Solid Films, 449, 1 (2004)
- 4. X. Zhang, Y. Hao, G. Meng, and L. Zhang, J. Electrochem. Soc., 152, C664 (2005).
- 5. R. Vaidyanathan, J. L. Stickney, S. M. Cox, S. P. Compton, and U. Happek, J. Electroanal. Chem., 559, 55 (2003).
- 6. R. Vaidyanathan, J. L. Stickney, and U. Happek, Electrochim. Acta, 49, 1321

(2004).

- 7. G. Leimkühler, I. Kerkamm, and R. Reineke-Koch, J. Electrochem. Soc., 149, C474 (2002).
- 8. C. Jin, G. Zhang, T. Qian, X. Li, and Z. Yao, J. Phys. Chem. B, 109, 1430 (2005). J. Yang, W. Zhu, X. Gao, S. Bao, X. Fan, X. Duan, and J. Hou, J. Phys. Chem. B, 9.
- 110, 4599 (2006).
- 10. Y. Miyazaki and T. Kajitani, J. Cryst. Growth, 229, 542 (2001).
- 11. A. Prabhakar, E. J. Podlaha-Murphy, M. C. Murphy, and R. V. Devireddy, in Proceedings of Material Research Society Symposium, Vol. 845, p. AA5.25 (2005).
- 12. M. Martín-González, A. L. Prieto, R. Gronsky, T. Sands, and A. M. Stacy, Adv. Mater., 15, 1003 (2003).
- 13. N. Romeo, A. Bosio, R. Tedeschi, A. Romeo, and V. Canevari, Solar Energy Mater. Solar Cells, 58, 209 (1999).
- F. J. Disalvo, *Science*, **285**, 703 (1999).
 L. van Pieterson, M. H. R. Lankhorst, M. van Schijndel, A. E. T. Kuiper, and J. H.
- J. Roosen, J. Appl. Phys., 97, 083520 (2005).
- 16. W. Shi, J. Yu, H. Wang, and H. Zhang, J. Am. Chem. Soc., 128, 16490 (2006).
- 17. S. S. Garje, D. J. Eisler, J. S. Ritch, M. Afzaal, P. O'Brien, and T. Chivers, J. Am. Chem. Soc., 128, 3120 (2006).
- 18. W. Wang, B. Poudel, J. Yang, D. Z. Wang, and Z. F. Ren, J. Am. Chem. Soc., 127, 13792 (2005).
- 19. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions, National Association of Corrosion Engineers, Houston, TX (1974).
- 20. J. E. E. Baglin, M. H. Tabacniks, and A. J. Kellock, Nucl. Instrum. Methods Phys. Res. B. 136-138, 241 (1998).
- 21. M. P. R. Panicker, M. Knaster, and K. A. Kroger, J. Electrochem. Soc., 125, 566 (1978).
- 22. K. K. Mishra and K. Majeshwar, J. Electroanal, Chem. Interfacial Electrochem. 271, 279 (1989).
- 23. J. Kois, S. Bereznev, E. Mellikov, and A. Öpìk, Thin Solid Films, 511-512, 420 (2006).
- 24. O. Younes and E. Gileadi, J. Electrochem. Soc., 149, C100 (2002).
- 25. E. J. Podlaha and D. Landolt, J. Electrochem. Soc., 143, 893 (1996) 26. Binary Alloy Phase Diagrams, 2nd ed., T. B. Massalski, Editor, ASM International, Materials Park, OH (1990).