University of Nebraska - Lincoln

DigitalCommons@University of Nebraska - Lincoln

Faculty Publications from Nebraska Center for
Materials and Nanoscience

Materials and Nanoscience, Nebraska Center
for (NCMN)

9-2011

Synthesis and characterization of highly textured Pt–Bi thin films

Xingzhong Li

University of Nebraska - Lincoln, xli2@unl.edu

Parashu Kharel

University of Nebraska - Lincoln, pkharel2@unl.edu

Shah R. Valloppilly

University of Nebraska-Lincoln, svalloppilly2@unl.edu

David J. Sellmyer

University of Nebraska-Lincoln, dsellmyer@unl.edu

Follow this and additional works at: <https://digitalcommons.unl.edu/cmrafacpub>

Part of the [Nanoscience and Nanotechnology Commons](#)

Li, Xingzhong; Kharel, Parashu; Valloppilly, Shah R.; and Sellmyer, David J., "Synthesis and characterization of highly textured Pt–Bi thin films" (2011). *Faculty Publications from Nebraska Center for Materials and Nanoscience*. 103.

<https://digitalcommons.unl.edu/cmrafacpub/103>

This Article is brought to you for free and open access by the Materials and Nanoscience, Nebraska Center for (NCMN) at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications from Nebraska Center for Materials and Nanoscience by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Synthesis and characterization of highly textured Pt–Bi thin films

X. Z. Li,¹ P. Kharel,^{1,2} V. R. Shah,¹ and D. J. Sellmyer^{1,2}

1. Nebraska Center for Materials and Nanoscience,
University of Nebraska–Lincoln, Lincoln, NE, 68588-0656, USA

2. Department of Physics and Astronomy,
University of Nebraska–Lincoln, Lincoln, NE, 68588-0656, USA

Corresponding author – X. Z. Li, xli2@unl.edu

Abstract

Pt–Bi films were synthesized on glass and thermally oxidized silicon substrates by e-beam evaporation and annealing. The structures were characterized using X-ray diffraction (XRD) and transmission electron microscopy/selected area electron diffraction (TEM/SAED) techniques. Single-phase PtBi was obtained at an annealing temperature of 300°C, whereas a higher annealing temperature of 400°C was required to obtain the highly textured γ -PtBi₂ phase. TEM/SAED analysis showed that the films annealed at 400°C contain a dominant γ -PtBi₂ phase with a small amount of β -PtBi₂ and α -PtBi₂ phases. Both the PtBi and γ -PtBi₂ phases are highly textured in these two kinds of film: the *c*-axis of the hexagonal PtBi phase is mostly in the film plane, whereas the *c*-axis of the trigonal γ -PtBi₂ phase is perpendicular to the film plane. The electrical resistivity of the film with the γ -PtBi₂ phase was smaller by one order of magnitude than that of the film with the PtBi phase.

Keywords: Pt–Bi, thin film, microstructure, texture, resistivity, XRD, TEM, electron diffraction, simulation

1. Introduction

There has been considerable interest in understanding various properties of Pt–Bi-based compounds because of their high activity as fuel-cell anode catalysts for formic acid (HCOOH) or methanol (CH₃OH) oxidation [1]. Although Pt is regarded as one of the most efficient catalyst materials, the main problem with this conventional catalyst is that it is readily poisoned by carbon monoxide (CO) that is produced as a side product of the reaction [2]. The CO poisoning reduces the catalytic activity and cell efficiency because it tends to remain strongly bound to the electrode surface. Although nanostructuring of the catalyst material is expected to exhibit superior properties such as high mass activity and improved resistance to CO poisoning [3], the chemical composition of the catalyst has been found to be another important factor that determines the catalytic activity [1]. Some recent reports show that the use of ordered intermetallic compound such as PtBi as an electrode material exhibits an improved cell efficiency with a dramatic reduction in the CO adsorption [2,4]. This has generated a great interest in the development of new cata-

lyst materials based on the compounds of Pt and Bi [5]. It has been found that the Pt-Pt interatomic distance in the Pt-Bi-based compounds is responsible in parts for the CO adsorption [6]. Thus, it is important to understand the detailed structural properties of the Pt-Bi-based compounds. In this paper, an experimental investigation is reported on the synthesis and characterization of nanocrystalline PtBi and PtBi₂ thin films. Our main focus is to understand the structural and electron transport properties of these nanocrystalline films.

The three common intermetallic compounds based on Pt and Bi are PtBi, PtBi₂ and Pt₂Bi₃. The equiatomic PtBi phase is on the low-temperature side of the phase diagram and may be off-stoichiometric towards Pt-rich side [7]. PtBi₂ has four polymorphs, namely α -PtBi₂ (oP24), β -PtBi₂ (cP12), γ -PtBi₂ (hP9) and δ -PtBi₂ (oP6) from low to high temperature in the equilibrium phase diagram [7]. PtBi and Pt₂Bi₃ adopt the hexagonal NiAs structure (PtBi: $a = 0.43240$ and $c = 0.5501$ nm; Pt₂Bi₃: $a = 0.413$ and $c = 0.558$ nm) whereas the polymorphs of PtBi₂ crystallize in the AuSn₂ type orthorhombic (α -PtBi₂: $a = 0.6732$, $b = 0.6794$ and $c = 1.3346$ nm), FeS₂ cubic pyrite (β -PtBi₂: $a = 0.6701$ nm), and trigonal (γ -PtBi₂: $a = 0.657$ and $c = 0.616$ nm) crystal structures, respectively [8–10]. We have found that highly textured PtBi and γ -PtBi₂ films can be grown on glass and silicon substrates by controlling the growth temperature and the chemical composition. Both PtBi and PtBi₂ films show metallic behavior but PtBi₂ films are more conducting than PtBi films.

2. Experiment

Pt-Bi thin films of total layer thicknesses of about 35 nm were prepared using an e-beam evaporation system. The samples were deposited at the lowest available base pressure of 2×10^{-8} Torr. Bi and Pt were deposited sequentially with Bi as the base layer on glass and silicon substrates at room temperature. We maintained a low deposition rate of 0.4 Å/s for both the elements. The Bi/Pt bi-layer samples (Sample A: 10.6 nm Pt and 24.8 nm Bi; Sample B: 6.2 nm Pt and 29 nm Bi) were annealed *in situ* at various temperatures. We were able to grow single phase PtBi in the hexagonal NiAs structure by annealing sample A at about 300°C. A higher annealing temperature of about 400°C was required to form the γ -PtBi₂ phase in sample B. The data presented here were taken on two samples A and B, which were annealed at 300°C and 400°C for one hour, respectively. The samples were slowly cooled to room temperature before being exposed to air outside the deposition chamber. The Pt to Bi atomic ratio was estimated from the corresponding layer thickness, which was determined using the quartz crystal thickness monitor. Energy dispersive X-ray spectroscopy (EDS) was used to confirm the chemical compositions in these samples. We used X-ray powder diffraction (XRD, Rigaku D/Max-B) and transmission electron microscopy/selected area electron diffraction (TEM/SAED, JEOL JEM2010 equipped with Oxford EDS detector) techniques to characterize the crystal structures and the chemical composition in the films. Electron diffraction simulations for single-crystalline and polycrystalline phase were carried out using JECPE/ED [11] software. Electrical transport properties were studied using the Quantum Design magnetic property measurement system (MPMS-XL) in conjunction with Keithley electrometers.

Figure 1. Experimental XRD pattern of sample A. All the peaks in the pattern are indexed to the hexagonal NiAs structure of PtBi. The calculated XRD pattern of the PtBi phase is shown below the experimental data for comparison. The most prominent reflection (102) greatly decreases and the reflection (103) is nearly absent in the film due to the development of texture.

3. Results and discussion

All XRD experiments were carried out at room temperature in θ - 2θ scanning mode. Figure 1 shows the XRD pattern for sample A. All the diffraction peaks in the pattern can be indexed with the standard peaks for the hexagonal NiAs structure of PtBi, although the strong peaks from (102) reflection at 40.75° greatly decreases and (103) reflection at 55.90° is nearly absent. The refined lattice parameters are very close to the values obtained from the ICDD database [13], and a calculated XRD pattern is shown below the experimental pattern for comparison. We find that the intensity decrease of the (102) and (103) reflections in the XRD pattern may be linked to the occurrence of the texture with the c -axis mostly lying in the film plane, e.g. the (110) or (100) orientation preference. The broad raised background below 45° is from the glass substrate. However, the presence of non-crystalline PtBi and elemental impurities contributing to this broad background cannot be completely ruled out.

Figure 2 shows the XRD pattern for sample B. The four peaks at 14.37° , 28.97° , 44.07° , and 60.03° correspond to the $(00\ n)$ ($n = 1, 2, 3, 4$) reflections of trigonal γ -PtBi₂. This indicates that the films exhibit a very high degree of texture having the crystallites oriented with the c -axis parallel to the film surface normal. The peak at 68.28° is identified as the (004) reflection from the PtBi minor phase. It is interesting to note that the PtBi minor phase also exhibits a high c -axis orientation, as evidenced by the presence of only (004) peak. The only peak of the highly (001) textured PtBi is the (004) reflection within a range of 70° . The observed c -axis texture is independent of the substrates we have used. We have been able to grow such highly textured γ -PtBi₂ films both on the glass and silicon substrates.

TEM specimens of sample A were prepared from the fragments of the films on glass substrates which were scratched down and transferred to a TEM Cu grid coated with ul-

Figure 2. Experimental XRD pattern of sample B. The first four peaks can be indexed as $(00\ n)$ ($n = 1, 2, 3, 4$) of the γ -PtBi₂ phase and the one at 68.28° as the (004) reflection of the PtBi phase. XRD patterns of the PtBi phase (second from top) and the γ -PtBi₂ phase (third from top) calculated without texture indicates the peak positions. The intensity mismatch between the calculated and experimental XRD patterns is due to the strong c -axis texture of γ -PtBi₂ and PtBi phases in the film.

Figure 3. TEM image of the fragments of the thin films, which were scratched down and transferred to a TEM Cu grid coated with ultrathin Carbon film. The films were deposited on glass substrates and *in situ* annealed at 300°C (sample A).

trathin carbon film. Figure 3 shows the TEM image of fragments from sample A. Since the fragments are rather thick and grain boundaries may not be revealed in the image, the average grain size of about 100 nm are estimated from some of the relatively thin isolated crystallites in the image. A careful analysis of chemical composition using EDS reveals that the Pt to Bi ratio in sample A is near 50:50, which is consistent with the PtBi phase. Although PtBi is reported to have a hexagonal structure, there are different views

Figure 4. Experimental polycrystalline SAED pattern of sample A (a) and the simulated ED pattern based on the structure of the PtBi hexagonal phase (b).

about the positions of its constituent atoms in the lattice. Zhuravlev and Stepanova [8] reported in the 1960 s that the PtBi adopts inverse NiAs structure with Bi at (0,0,0) and Pt at $(1/3, 2/3, 1/4)$ positions and the lattice parameters are $a = 0.4340$ nm and $c = 0.5493$ nm. However, Casado-Rivera et al. [2] recently analyzed high-quality X-ray powder diffraction data to refine the positions of Pt and Bi in the PtBi lattice and found that the NiAs structure for PtBi is more plausible than the inverse NiAs structure. In the NiAs structure, Pt and Bi occupy the (0,0,0) and $(1/3, 2/3, 1/4)$ positions, respectively. Our study is also consistent with the later argument supporting the NiAs structure of PtBi.

Figure 4a shows the polycrystalline SAED pattern of sample A and Figure 4b the diffraction pattern simulated for PtBi assuming the hexagonal NiAs prototypical structure. The radii and relative intensities of the simulated reflection rings are in good agreement with that of the experimental data. In combination of the results of the XRD analysis above, we conclude that our samples adopt the hexagonal NiAs structure. Our simulation yields a Pt–Pt interatomic distance of 0.2745 nm and Pt–Bi distance of 0.2844 nm, which are close to the values reported previously in the literature [2].

Figure 5. TEM image of sample B deposited on Si substrate and annealed at 400°C. The fine structures in the grains are marked with arrows.

As mentioned above, the PtBi_2 samples were prepared both on glass and thermally oxidized silicon substrates. Both the samples have identical XRD and SAED patterns. Figure 5 shows the TEM image of sample B deposited on silicon substrate. The grains have a wider size distribution with the average grain size of about 200 nm. The fine structures of the planar defects and/or twinning are marked with arrows. The chemical composition determined from the EDS analysis shows a Pt to Bi average ratio of 33 to 67 supporting the PtBi_2 phase in the samples.

In order to better understand the crystal structure, accurately identify the structural phases and precisely determine the presence of elemental or alloy impurities, we have analyzed SAED patterns recorded at different parts of the specimen with a series of sample tilt angles. Here we present SAED patterns recorded at two different parts of the specimen (see Figures 6 and 7). We have found that the samples contain a mixture of the $\alpha\text{-PtBi}_2$, $\beta\text{-PtBi}_2$ and the $\gamma\text{-PtBi}_2$ phases, although the XRD patterns show only the $\gamma\text{-PtBi}_2$ due to the strong texture of the $\gamma\text{-PtBi}_2$ crystallites.

Figures 6a and c show the SAED patterns recorded on the same grain of sample B with different sample tilt angles. The corresponding simulated patterns for the $\gamma\text{-PtBi}_2$ are shown in Figures 6b and d, respectively. The agreement between the electron diffraction patterns simulated for the $\gamma\text{-PtBi}_2$ and the experimentally recorded SAED patterns indicates that sample B mostly consists of the $\gamma\text{-PtBi}_2$. The PtBi_2 lattice simulated for its γ -phase yields a Pt-Pt interatomic distance of 0.3827 nm and Pt-Bi distance of 0.2748 nm. However, a closer look at the experimental pattern shows that the sample B also contains a small amount of the hexagonal PtBi phase. As marked by the arrows in Figures 6a and c, the weak rings correspond to PtBi in the hexagonal structure. This is consistent with the presence of the PtBi (004) in the XRD pattern. We have found that there is an orientation relationship between the $\gamma\text{-PtBi}_2$ and the PtBi phases with $[001]$ of the $\gamma\text{-PtBi}_2$ // $[001]$ of the PtBi and (100) of the $\gamma\text{-PtBi}_2$ // (110) of the PtBi.

Figure 6. Experimental SAED patterns of sample B (a, c) and simulated ED patterns based on the structure of the γ -PtBi₂ phase (b, d). The strong diffraction spots marked with thick arrows in (a) and (c) correspond to the lattice of γ -PtBi₂ phase, whereas the weak diffraction spots correspond to the lattice of the PtBi phase. The weak diffraction spots from PtBi phase are indexed in (a) and (c), whereas the strong diffraction spots from the γ -PtBi₂ phase are indexed in the corresponding simulated patterns in (b) and (d), respectively.

Figures 7a and c show the SAED patterns recorded with different tilt angles at another crystal of the specimen prepared from sample B. These patterns are different from the patterns simulated for the γ -PtBi₂ phase. However, the experimental patterns (Figures 7a and c) are consistent with the corresponding patterns (Figures 7b and d) simulated for the β -PtBi₂ phase. A closer look at the experimental patterns of Figures 7a and c gives an impression of doubling of the vertical axis with weak and bright spots. We have found that the weak spots originate from the orthorhombic α -PtBi₂ phase. The orthorhombic α -PtBi₂ and cubic β -PtBi₂ phases have a close structural relationship: the a and b lattice parameters of the former are close to the lattice parameter of the latter, whereas the c lattice parameter of the former is almost twice that of the latter. The fixed orientation relationship

Figure 7. Experimental SAED patterns of sample B (a, c) and simulated ED patterns based on the structure of the β -PtBi₂ phase (b, d). The vertical axis in (a) and (c) consists of two sets of diffraction spots of different intensities. The strong spots marked with thick arrows correspond to the β -PtBi₂ lattice and the weak spots marked with thin arrows are from the α -PtBi₂ lattice. The strong diffraction spots from β -PtBi₂ phase are indexed in (b) and (d). The lack of *mm*-symmetry in (c) is due to a slight crystal misalignment.

between the α -PtBi₂ and β -PtBi₂ phases exists with their three axes all parallel with each other in the two phases. The PtBi₂ lattice simulated for its β -phase yields the Pt-Pt interatomic distance of 0.4739 nm and Pt-Bi distance of 0.2771 nm. But no trace of PtBi was found in this crystal. We believe that the intensities of α -PtBi₂ and β -PtBi₂ are suppressed in the XRD pattern due to the presence of strong texture of γ -PtBi₂.

Electron transport measurements were carried out in the van der Pauw configuration using MPMS-XL and Keithley electrometers. Figure 8 shows the electrical resistivity (ρ_{xx} or simply ρ) as a function of temperature for samples A and B. The resistivities of the samples measured between 2 K and 300 K have an identical temperature dependence and are metallic. We have found that the resistivity of sample B, annealed at 400°C, is about

Figure 8. Resistivities of the samples A (scale on the left) and B (scale on the right) as a function of temperature between 2 K and 300 K. The measured resistivities of both the samples show an almost identical temperature dependence. We have used the total film thicknesses of the annealed samples (29 nm for sample A and 30 nm for sample B) to calculate their resistivities.

one order of magnitude smaller than that of the sample A, annealed at 300°C. The residual resistivity of sample A is $3.8 \times 10^{-4} \Omega \text{ cm}$ and that of the sample B is $2.0 \times 10^{-5} \Omega \text{ cm}$. Although the details about the mechanism of electron transport in PtBi and PtBi₂ are not clear at this point, the higher electrical conductivity in PtBi₂ may be partly attributed to the larger grain size in the sample, which is consistent with our TEM results. However, as mentioned above, sample A annealed at the lower substrate temperature may contain elemental impurities and non-crystalline PtBi compound and can contribute to the resistivity of sample A. On the other hand, the residual resistance ratio defined as $\text{RRR} = \rho_{300\text{K}} / \rho_{4\text{K}}$ is slightly higher for the sample B. It is 2.2 for the sample A and 2.7 for sample B. Although sample B consists of a small trace of the PtBi phase, the observed high conductivity indicates that the PtBi₂ compounds annealed at higher temperatures can serve as a better electrode material because the electrodes with low-resistance are preferred to minimize the ohmic loss.

4. Conclusion

We have prepared PtBi and PtBi₂ films by multilayer deposition and annealing using e-beam evaporation technique. XRD and TEM/SAED analysis show that single phase PtBi can be grown at lower annealing temperature of 300°C but the polymorphic PtBi₂ phases can be obtained at an annealing temperature of 400°C. Although we have been able to synthesize single phase hexagonal PtBi at 300°C annealing temperature, the samples annealed at 400°C consist of mostly trigonal γ -PtBi₂ and also a small amount of orthorhombic α -PtBi₂, cubic β -PtBi₂ and hexagonal PtBi. These phases are distributed unevenly in the sample. Some crystallites show γ -PtBi₂ with small amount of PtBi impurity phase and others show only the mixture of α -PtBi₂ and β -PtBi₂ phases. Both the PtBi and PtBi₂ samples are highly textured: the *c*-axis in the former is in the film plane, whereas that of the latter is perpendicular to the film plane. The PtBi and the γ -PtBi₂ phases in

the PtBi₂ sample show a structural relationship where [001] of γ -PtBi₂//[001] of PtBi and (100) of γ -PtBi₂//(110) of PtBi. The simulation of the structures shows that the Pt-Pt interatomic distance in PtBi₂ is larger than that in PtBi phase. Electrical resistivity measurements between 2 K to 300 K show that both the PtBi and PtBi₂ films are metallic but that PtBi₂ is a better conductor than PtBi. Since the increased Pt-Pt distance in Pt–Bi intermetallic compounds is believed to be responsible in part for the reduction of CO adsorption, PtBi₂ compounds having lower electrical resistivity can serve as the better candidates for electrode materials.

Acknowledgments — This work was supported by the NSF-MRSEC (Grant DMR-0820521), the DOE grant DE-FG02-04ER46152 (P.K. and D.J.S.), and NCMN.

References

1. Ji, X, Lee, KT, Holden, R, Zhang, L, Zhang, J, Botton, GA, Couillard, M and Nazar, LF. 2010. *Nat. Chem.*, 2: 286
2. Casado-Rivera, E, Gál, Z, Angelo, ACD, Lind, C, Disalvo, FJ and Abruña, HD. 2003. *Chem. Phys. Chem.*, 4: 193
3. Roychowdhury, C, Matsumoto, F, Zeldovich, VB, Warren, SC, Mutolo, PF, Ballesteros, M, Wiesner, U, Abruña, HD and DiSalvo, FJ. 2006. *Chem. Mater.*, 18: 3365
4. Oana, M, Hoffmann, R, Abruña, HD and DiSalvo, FJ. 2005. *Surf. Sci.*, 574: 1
5. Xia, D, Chen, G, Wang, Z, Zhang, J, Hui, S, Ghosh, D and Wang, H. 2006. *Chem. Mater.*, 18: 5746
6. Casado-Rivera, E, Volpe, DJ, Alden, L, Lind, C, Downie, C, Vázquez-Alvarez, T, Angelo, ACD, Disalvo, FJ and Abruña, HD. 2004. *J. Am. Chem. Soc.*, 126: 4043
7. Okamoto, H. 1991. *J. Phase Equil.*, 12: 207
8. Zhuravlev, NN and Stepanova, AA. 1962. *Sov. Phys. Crystallogr.*, 7: 241
9. International Center for Diffraction Data, PDF 03-065-8738, 2010
10. Kjekshus, A. 1960. *Acta. Chem. Scand.*, 14: 1450
11. Li, XZ. 2003. *J. Appl. Crystallogr.*, 36: 956
12. Li, XZ. 2010. *Ultramicroscopy*, 110: 297
13. International Center for Diffraction Data, PDF 04-007-4117, 2010