Electrodeposition of Single-Crystal Cubes of Lead Telluride on Polycrystalline Gold Substrate

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Single-crystal cubes of lead telluride (PbTe with NaCl structure) were electrodeposited on polycrystalline gold substrates. Electron and X-ray diffraction patterns and high-resolution TEM confirm that the single-crystal PbTe cubes were grown with their \{100\} planes parallel to the surface of the gold seed layer. The PbTe cubes might have nucleated on the \{100\} faces of individual Au grains on the basis of lattice mismatch calculation, followed by the lateral growth of new layers on the nuclei along the \{110\} directions from the four edges of the PbTe cubes. The enlargement of the PbTe single crystals occurred through lateral growth, which led to the development of relatively large single-crystal cubes on polycrystalline Au seed layers having a smaller grain size.

Introduction

A single crystalline film is a very important for device fabrication because the film has fewer structural defects as compared to a polycrystalline film. Epitaxially grown single crystalline films are generally fabricated by vacuum vapor deposition onto a single crystalline substrate. To minimize defect formation, substrates with a similar crystal structure and lattice constants as well as thermal expansion coefficient are chosen.1

Several methods have been used to achieve epitaxial growth of film, including molecular beam epitaxy,2 chemical vapor deposition,3 chemical bath deposition,4,5 underpotential electrodeposition,6,7 and overpotential electrodeposition.8–10 Compared to vacuum vapor depositions, electrodeposition is a simple, cost-effective, scaleable, and fast wet process which allows precise control of the composition, crystallographic structure, texture and grain size.

Lead telluride (PbTe) is a narrow band gap (≈0.31 eV) semiconductor with a rock-salt crystal structure. Because of high quantum efficiencies, a low noise level at working temperature, and an ability to tune the peak wavelength by adjusting the alloy composition,11,12 PbTe is a great candidate material for infrared (IR) optoelectronics devices (e.g., IR detector and mid-infrared quantum well laser diode). In addition, PbTe is among the most efficient thermoelectric materials in the intermediate range of quantum efficiencies, a high melting point, good chemical stability, cost-effective, scaleable, and fast wet process which allows precise control of the composition, crystallographic structure, texture and grain size.

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In this paper, we report electrodeposition of single-crystal cubes of PbTe on a polycrystalline gold substrate from a nitric acid bath containing $5 \times 10^{-2}$ M Pb$^{2+}$, $1 \times 10^{-4}$ M HTeO$_2^-$, and 1 M HNO$_3$. PbTe single-crystal cubes are of great interest because they can possess higher collection efficiency and better photoconductive properties.

Experimental Methods

PbTe was electrodeposited from acidic nitric acid electrolytes. TeO$_2$ (99.9995%; Alfa Aesar, Inc.) and Pb(NO$_3$)$_2$ (99.1%; Fisher Scientific) were dissolved in HNO$_3$ and diluted with deionized water to make a solution, the ion concentration of which was $1 \times 10^{-4}$ M HTeO$_2^-$ and $5 \times 10^{-3}$ M Pb$^{2+}$ with 1 M of HNO$_3$. Working electrodes were 1 cm$^2$ evaporated Au thin films on (100) oriented silicon wafers. The Au seed layers had (111) preferred orientation. To confirm the preferential nucleation of PbTe on the Au\{100\} plane, a (100)-oriented, single-crystal Au plate (9.5 mm × 1 mm, Electronic Space Product International, Inc.) was also used as the working electrode. The electrodeposition was carried out at a fixed potential of $-0.12$ V with respect to a Ag/AgCl reference electrode (in saturated KCl) and a platinum-coated titanium sheet counter electrode by EG&G Princeton Applied Research (PAR), model Verstat II Multi-Potentio/Gavalnostat. A 200 mL aliquot of deposition solution was magnetically stirred at 300 rpm at room temperature. Prior to electrodeposition, linear sweep voltammetry (LSV) was performed with the same cell to investigate the electrochemical reactions. The scan rate was fixed at $-10$ mV/s. In addition to LSV, chronoamperometry was conducted to determine the nucleation and growth behavior of the PbTe deposits. The crystal orientation of the deposits was determined by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu Ka radiation. Scanning electron microscopy (SEM, LEO 1550 VP FESEM) and atomic force microscopy (AFM, PSIA XE-100) were used for investigation of the surface morphology. High-resolution lattice images and selected area electron diffraction patterns were obtained with a transmission electron microscope (TEM), FEI CM300, at an accelerating voltage of 300 kV with a point-to-point resolution.

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of 2.3 Å. Samples were prepared by scraping crystals from the Au substrate and depositing them on holey carbon Cu grids.

**Results and Discussion**

In our previous studies, we reported that PbTe thin films can be potentiostatically electrodeposited by underpotential deposition (UPD) of Pb onto first overpotentially deposited Te.\(^\text{17}\) Figure 1a shows a linear sweep voltammogram (LSV) for PbTe electrodeposition. When the potential was negatively swept to $\sim -0.05$ V vs a Ag/AgCl electrode, a reduction peak started to appear, which was caused by the deposition of elemental Te. Further decreasing of the deposition potential to $\sim -0.11$ V enhanced the reduction current due to underpotential deposition of Pb onto first deposited Te. The overall electrodeposition of PbTe can be represented by the following electrochemical reactions:

\[
\text{HTeO}_2^+ + 3\text{H}^+ + 4\text{e}^- \rightarrow \text{Te}_{(\text{ads})} + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{Pb}^{2+} + \text{Te}_{(\text{ads})} + 2\text{e}^- \rightarrow \text{PbTe} \quad (2)
\]

where Te\(_{\text{(ads)}}\) represents reduced tellurium atoms absorbed on the Au seed layer. As the potential reached $\sim -0.3$ V, another reduction wave started to develop, which could be attributed to the generation of H\(_2\)Te.\(^\text{18}\) Overpotential deposition of Pb started at $\sim -0.43$ V, which is not shown.

On the basis of the linear sweep voltammogram, a reduction deposition potential of $-0.12$ V vs Ag/AgCl, which is the initial point for the UPD of Pb on Te, was selected to acquire stoichiometric PbTe deposits. Figure 1b shows the current transient of PbTe electrodeposition at $-0.12$ V. Initially, the current density drastically decreased to $-0.16$ mA/cm\(^2\), which corresponds to the establishment of a double layer near the surface of the working electrode.\(^\text{19}\) After a short deposition time, the current density fluctuated, establishing several peaks with different wavelengths. By comparing the first peak labeled as “A” with the theoretical calculation based on BFT theory,\(^\text{20}\) it

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**Figure 1.** (a) Linear sweep voltammogram and (b) chronoamperogram of PbTe electrodeposition, in electrolytes containing $1 \times 10^{-4}$ M H\(_{\text{TeO}}^2\), $5 \times 10^{-2}$ M Pb\(^{2+}\), and 1 M HNO\(_3\).

**Figure 2.** (a) SEM micrographs of PbTe deposits after 2 min depositions at $-0.12$ V vs Ag/AgCl. The inset images provide tilted view at higher magnification. (b) The corresponding HRTEM image of the single crystalline PbTe deposit, obtained after tilting the crystal from a horizontal orientation to attain relatively thin edges transparent to the electron beam. (c) \(\langle 011 \rangle\) zone axis electron diffraction pattern of the PbTe deposit.
was concluded that the nucleation of PbTe at this deposition potential was two-dimensional progressive nucleation and growth. In addition, increasing the wavelength of each peak with an increase in the deposition time suggested that the overlap of nucleation of PbTe occurred as the deposition proceeded. Such a result from the current transient strongly implied that PbTe crystals were synthesized with two-dimensional lateral growth from discrete nucleation sites. To confirm this, morphologies of PbTe deposits with ~0.12 V vs Ag/AgCl were investigated with SEM.

The typical morphology of PbTe after 2 min of electrodeposition is shown in Figure 2a. As shown, instead of growing a conformal continuous thin film, preferentially oriented cubes were observed. Such a morphology was very reproducible on the polycrystalline gold substrate; however, it could not be obtained on other polycrystalline substrates (e.g., Pt and Cu) or from more concentrated electrolytes.\(^{17}\) The average width of the cube was ~340 nm, and the average height was ~180 nm.

CVD growth of single-crystal semiconductors with a whisker or nanowire shape is well-known,\(^{20,21}\) but in these cases, a specific catalyst is needed to initiate the growth. In our study, individual single crystalline cubes were grown on top of the evaporated polycrystalline Au seed layer by electrodeposition without any catalyst.

To analyze the obtained cubes, several investigations were carried out. First of all, the composition of these deposits was confirmed by energy dispersive spectroscopy, which indicated the formation of stoichiometric PbTe. The crystal structure of these cubes was analyzed by the select-area electron diffraction, which was obtained after tilting the crystal from the horizontal face. All of the analyzed cubes generated dotted electron diffraction patterns, and twins and rotation growth were not observed. A typical electron diffraction pattern of the [011] zone axis is shown in Figure 2c. The dotted electron diffraction pattern confirmed that individual cubes were perfect single crystals of PbTe with face centered cubic (fcc) structure and lattice parameter \(a = 6.459\) Å. The lattice fringes shown in HRTEM image (Figure 2b) confirm the perfect order of the crystalline lattice of the PbTe cube. The spacing of 0.322 and 0.373 nm corresponds to the \{200\} and \{111\} planes of the fcc PbTe, respectively. To corroborate the structure and crystal orientation, XRD analysis was performed. Figure 3a shows the X-ray diffraction patterns of PbTe deposits. It clearly shows that PbTe deposits have a strong \{100\} preferred orientation on the Au seed layers, which had \{111\} preferred orientation.

Dependence of the number and the size of PbTe cubes on the deposition time are shown in Figure 3b. As the deposition time increased from 2 to 50 min, PbTe cubes did not develop into a thin film structure; rather, the individual cubes were continuously enlarged (width: ~340 nm (2 min) to ~720 nm (50 min)), while the number of individual cubes ceased to increase after 20 min (~0.39 \( \times 10^5 \) cm\(^2\) at 2 min to ~1.77 \( \times 10^5 \) cm\(^2\) at 20 min), which indicates that the nucleation of PbTe on the Au substrate occurred continuously during deposition, following the progressive nucleation mechanism. After 20 min, the number of PbTe cubes increased very slowly. XRD results of PbTe deposits with different deposition time (20 min) show that up to a deposition time of 20 min, only \{200\} reflections are observed. However, when the deposition time reached 50 min, the PbTe (220) peak became visible, which might be caused by formation of dendritic growth of PbTe on top of PbTe cubes.

![Figure 3](image)

**Figure 3.** (a) XRD patterns of PbTe deposited with different deposition times (2, 10, 20, and 50 min). (b) Number of PbTe cubes and average cube width at various deposition times.

<table>
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<th>TABLE 1: Calculated Lattice Mismatch between the PbTe {100} Plane and (a) Au {111}, (b) Au {110}, and (c) Au {100} Planes at the Distance of the Unit Cell and Minimum Mismatched Superlattice</th>
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According to the analysis results from SEM, TEM, and XRD, it is clear that the individually grown single-crystal PbTe cubes are oriented with their \{100\} planes parallel to the surface of the polycrystalline Au thin films, which have an average grain size of ~80 nm. It is very unusual that large single crystals can be grown on a polycrystalline substrate with a much smaller...
grain size. In our experiment, PbTe single crystals with lateral dimensions of almost 1 µm were obtained on a Au substrate having 80 nm grain size. This fact suggests that independently grown single crystals attain their equilibrium shape under specific nucleation and growth conditions.

To derive the possible deposition mechanism of single crystalline PbTe cubes, proper nucleation sites for epitaxial growth of PbTe must be identified. As shown in Figure 3a, the \{111\} are the dominant planes of the Au parallel to the substrate. However, if \{111\} planes were considered as the nucleation sites, it is difficult to explain the comparably low number of nuclei on the Au thin film. If it is assumed that each nucleation event could initiate on an individual Au grain, then the specific number of Au grains that would allow the formation of the observed maximum number of PbTe nucleation sites should be ~1.77 × 10^9/cm^2, as shown in Figure 3b, which is only ~1.4% of the total number of Au grains (average grain diameter of the evaporated Au thin film at the surface = ~80 nm). Since the Au substrate exhibits clearly \{111\} preferred orientation, it is obvious that much more than 1% of the Au grains are oriented with the \{111\} parallel to the substrate. Therefore, \{111\} as the dominant plane of the Au cannot be considered as a proper nucleation site, since the number of PbTe nuclei was very much smaller than the potentially available Au crystals with \{111\} surfaces. The XRD signal could not detect any other reflections of Au apart from \langle111\rangle (Figure 3a), which further suggests that probably well over 90% of the surface is formed by \{111\} preferentially oriented Au crystals. The remaining very small portion of the Au crystals with appropriate orientation might have acted as nucleation sites for PbTe.

To investigate which plane in Au could be the best candidate for the epitaxial growth of PbTe, the lattice mismatch between possible low index planes of Au, such as \{111\}, \{100\}, and \{110\}, and PbTe[100] were examined. Calculated mismatches

Figure 4. Schematic illustration of single crystalline PbTe cube formation on polycrystalline gold substrate. (a) PbTe nuclei selectively generated on a Au \{100\} plane with the \{100\} plane parallel to the surface. (b) Growth of PbTe nuclei initiates from four edges on PbTe nuclei. (c) Additional planes begin to grow laterally with the \langle110\rangle direction on the surface of the PbTe. (d) Other layers laterally grow from the four edges on PbTe. (e) Growth of PbTe initiates at the top edges of the PbTe to laterally and downward so that its orientation would not affected by the orientation of neighboring Au grains. (f) Additional layers begin to grow laterally before the underlayers fully cover the PbTe surface. (g) SEM image of a fully developed single crystalline PbTe cube after 50 min.
suggests that the three mismatch percentages adds up to 32.4%. This clearly not exceed 10.8% in all three directions, and the sum of all mismatches between the Au in the disposition of the atoms at the interface; the same is true for the mismatch was calculated as the percentage of the absolute difference between the vector lengths of corresponding rows of atoms. The {100} interface of PbTe is defined by square disposition of the atoms at the interface; the same is true for Au in the {100} orientation. The {110} Au orientation is defined by a rectangular primitive unit cell, whereas the {111} Au interface is defined by hexagonal atom disposition, which can be described also by a rectangular centered unit cell. In addition, the possible closest matching superlattices in each orientation are defined, and the respective mismatches along the sides and diagonals of the superlattice unit cells are calculated.

For example, in the orientation where PbTe{100} is parallel to Au {111}, {100}, and {110} are represented in Table 1 as the percent mismatch between the interatomic distances along major directions in both structures parallel to each other in the specified interface. In each case, a two-dimensional unit cell was defined for each interface, as listed in Table 1. The directions shown are the lattice vectors parallel to the specific row of atoms. The first two vectors define the sides of the unit parallelogram, and the third one is the diagonal of the unit cell defined by the first two vectors. The mismatch was calculated as the percentage of the absolute difference between the vector lengths of corresponding rows of atoms. The {100} interface of PbTe is defined by square disposition of the atoms at the interface; the same is true for Au in the {100} orientation. The {110} Au orientation is defined by a rectangular primitive unit cell, whereas the {111} Au interface is defined by hexagonal atom disposition, which can be described also by a rectangular centered unit cell. In addition, the possible closest matching superlattices in each orientation are defined, and the respective mismatches along the sides and diagonals of the superlattice unit cells are calculated.

In the case when the Au {110} planes are considered parallel to the interface, respectively as nucleation sites, interpretations analogous to the above suggest that the mismatch in the PbTe (100) direction, which could be parallel to the Au (100), sums to 46.5%. Unlike the {111} and {110} planes, the lattice mismatches between the Au{100} and PbTe{100} planes do not exceed 10.8% in all three directions, and the sum of all three mismatch percentages adds up to 32.4%. This clearly suggests that the {111} Au interface parallel to the {100} PbTe will generate about three times more repulsive energy as compared to the {100} Au parallel to the {100} PbTe. These speculations strongly imply that the Au{100} plane should be the best candidate for a nucleation site for stable epitaxial growth of PbTe {100}. When a superlattice structure is considered, the lattice mismatch of PbTe {100} and Au {100} would be reduced to 1.05%, when a 4 × [100] by 4 × [001] PbTe superlattice is superimposed on a Au 4.5 × [110] by 4.5 × [1-10], even though a higher stress could exist within the superlattice structure. XRD results did not show any peak from the {100} plane, which means that the density of the Au crystals with a {100} plane parallel to the interface would be very low for detecting. This observation is consistent with the small number of saturated nucleation sites for PbTe, which was only ~1.4% and, thus, will not be detectable by XRD. To verify this hypothesis that Au {100} planes would be the suitable nucleation sites for growing of PbTe single crystals, PbTe was deposited on a {100} oriented single-crystal Au sheet. Conformal continuous thin films were deposited on the substrate at a faster deposition rate as compared to an e-beam-evaporated gold film. X-ray diffraction patterns confirmed the presence of a single PbTe {100} peak on a (100) oriented single-crystal Au sheet (data not shown).

On the basis of the above observation, a suitable deposition mechanism was suggested in Figure 4. As discussed previously, it can be conjectured that the nucleation of each PbTe cube is initiated on a single Au grain that has a {100} plane, parallel to the substrate (indicated as “A” in Figure 4). After nucleation, the growth of the nucleus proceeds as new planes start to grow laterally from each top corner of the cube which lie on the {111} direction of the PbTe single crystal (Figure 4b). The direction of lateral growth of each new plane must be along the {110} direction with developing {100} faces as a consequence. It means that growth of PbTe, by absorbing the
new ions, occurred only at the surface of the PbTe cubes so that the orientation of the neighboring Au grains would not affect the growth of the PbTe deposits. The direction and shape of sharp steps on the surface of PbTe, which must be the consequence of unfinished expanding of laterally growing planes, are strong evidence that the lateral growth of [100] PbTe planes would be initiated from the four corners of the cube and will grow along the ⟨110⟩ directions (Figure 4g).

The detail surface topology occurred by laterally growing planes confirmed by AFM profiling, as shown in Figure 5. The height of the steps confirmed by AFM was ~4 to 12 nm, which is far larger than the atomic distance of PbTe (4.576 Å). It can be explained that the lateral growth did not occur at the atomic layer level, but a few atomic layers are laterally grown simultaneously.

The coalescence of deposits during the growth of nuclei could be minimized by a low nucleation rate. The nucleation rate in electrodeposition is highly dependent on the applied potential, and −0.12 V vs Ag/AgCl, which is the potential applied in our work, is a relatively low potential so that the nucleation rate became low enough to minimize the density of the nuclei. The growth of the nuclei seems to be also governed by kinetic control because of a low applied potential, which is a crucial condition for acquiring epitaxial growth; therefore, the crystal orientation of the eposis is highly affected by the substrate.\(^{22}\)

Conclusions

We electrodeposited single crystalline PbTe cubes on a polycrystalline gold substrate from acidic nitric electrolytes by applying a deposition potential of −0.12 V vs Ag/AgCl. Such a low deposition potential caused a low nucleation rate and kinetic control growth of PbTe deposits; thus, single crystals of PbTe have been preferentially nucleated on a Au[100] plane, which caused the lowest mismatch with the [100] face of PbTe. After nucleation, the growth of nuclei proceed with laterally expanding new planes from each of the top corners of the cubes, which is the ⟨110⟩ direction of PbTe single crystals.

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References and Notes