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TEM Investigation of Bi₂Te₃/Sb₂Te₃ Nanolaminate Structures Synthesized by Atomic Layer Deposition

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High efficiency thermoelectric materials have been extensively investigated due to their potential application in power generation and refrigeration systems. The efficiency of thermoelectric materials is expressed by the figure of merit (ZT), $ZT = S^2 \sigma T / (\kappa_l + \kappa_e)$, where S is Seebeck coefficient, σ is electrical conductivity, T is the absolute temperature, and $\kappa_l + \kappa_e$ are the thermal conductivity due to the lattice and electron contribution. It is observed that higher thermoelectric efficiency can be obtained by increasing the electron conductivity and reducing the thermal conductivity. A decrease of thermal conductivity could be achieved by a low dimensional superlattice structure, due to the quantum confinement or phonon scattering. In the past Bi₂Te₃/Sb₂Te₃ superlattice nanostructures have been attempted by using conventional techniques, such as pulsed laser deposition (PLD), metal-organic chemical vapor deposition (MO-CVD), and molecular beam epitaxy (MBE) at high temperature. However, high growth temperature results in the issues of interlayer outdiffusion and thermal lattice mismatch, which in turn adversely affects the thermoelectric performance. In contrast, the growth temperature of ALD is rather low in comparison with other thin film fabrication processes. In this paper we report on the fabrication of thermoelectric superlattice nanolaminate structures of alternating Bi₂Te₃ and Sb₂Te₃ ALD layers.

Trimethylsilyl telluride ((Me₃Si)₂Te), bismuth trichloride (BiCl₃) and antimony trichloride (SbCl₃) were utilized as chemical ALD precursors for telluride, bismuth and antimony, respectively. The results of field emission scanning electron microscopy (FE-SEM) indicate both metal tellurides exhibit the prevalent Volmer-Weber island growth mechanism with characteristic hexagonal crystallites revealing telluride-terminated surfaces. It is found that the addition of hydroxyl OH⁻ bonds at the native Si oxide surface of the substrate promotes ALD growth of metal tellurides by providing suitable nucleation sites and by preventing delamination of the hexagonal platelet shaped crystallites. The use of longer ALD pulse exposure times of chemical precursors during the ALD process enhances chemisorption and the number of nucleation sites. During subsequent ALD growth the individual nucleated islands coalesce into a continuous layer with smooth surface morphology. Transmission electron microscopic (TEM) studies (FEI Titan80-300) were performed to analyze the ALD deposited nanolaminate material. Cross-sectional analysis of these materials confirmed the Volmer-Weber type growth mechanism.

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First high resolution transmission electron microscopy characterization of fcc \rightarrow 9R transformation in nanocrystalline palladium films due to hydriding

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Thin palladium (Pd) membranes constitute an enabling material in hydrogen permeation and sensing applications essential for hydrogen energy technology. These membranes must be as thin as possible to ensure high hydrogen permeability while remaining mechanically stable. It has been recently reported that the ductility of Pd thin films with an average grain size of 30 nm can be significantly improved due to the presence of coherent growth nanotwins [1].

In the present work, nanocrystalline (nc) Pd films with 150 nm thickness containing nanoscale growth Σ 3{111} coherent TBs (CTBs) and Σ 3{112} incoherent TBs (ITBs) were produced using sputter deposition and subjected to hydriding cycles. Figure 1(a) is a BF image of a plan-view FIB sample of the as-sputtered Pd film. The average in-plane grain size equals 26 ± 1 nm while the cross-sections reveal a columnar morphological texture with an average elongated aspect ratio (height/lateral dimension ratio) of 3. Growth nanotwins are indicated by white arrows in Figure 1(a). In Figure 1(b), a $\langle 110 \rangle$ HRTEM image of a single grain is shown in which parallel Σ 3{111} CTBs connected by Σ 3{112} ITBs are recognized. The incoherent character of the Σ 3{112} ITBs can be clearly distinguished in the Geometrical Phase Analysis (GPA) map of Figure 1(c) with an array of misfit dislocations located at the Σ 3{112} ITBs. Figure 1(d) shows the evolution of the internal stress as a function of time during a complete hydriding cycle at $P_{H_2} = 97.5$ mbar. This pressure is large enough to induce the $\alpha \rightarrow \beta$ transformation in nc Pd. The initial volume of the Pd structure expands by about 10% during this phase transformation [2], which induces a plastic deformation within the Pd film.

After a hydriding/dehydriding cycle of Pd films, it was observed that Σ 3{112} ITBs dissociate into two phase boundaries bounding a new and thermodynamically unstable 9R phase with the formation of single stacking faults every three {111} planes. Figure 2(a) shows a $\langle 110 \rangle$ oriented HRTEM micrograph of a straight band exhibiting two common {111} interfaces bounding a 9R phase in a hydrided Pd sample. However, care needs to be taken not to confuse a genuine 9R area with an overlapping region between twin and matrix, also causing an extra threefold periodicity in the $\langle 110 \rangle$ HRTEM images of an fcc lattice. The difference between both cases can be observed from the actual position of these 1/3 extra spots in the first rows next to the central $\langle 111 \rangle$ row. By analysis of the Fast Fourier Transform (FFT) of the HRTEM images, for a true 9R structure, observed along a $\langle 110 \rangle_{fcc}$ direction, none of the spots in these rows coincides with the center normal to the $\langle 111 \rangle$ long period axis, as seen in the example of Figure 2(a). On the other hand, for the overlapping case, this normal crosses the middle spot in the adjacent row, as seen in Figure 2(b).

The sizes of the observed 9R regions and thus the dissociation width of the Σ 3{112} ITBs are in the 5 to 30 ± 1 nm range. Figure 3(b) shows an example of a smaller 9R region after hydriding indicating that not all regions involve extended dissociation. Figure 3(c) exhibits a GPA map of the region indicated by solid lines in Figure 3(b); the misfit dislocations located at the two 9R phase boundaries can be clearly observed. In the area indicated by dashed lines in Figure 3(b), the exact stacking is revealed from the HRTEM lattice micrograph, further enlarged in Figure 3(d) and which exhibits some stacking defects (due to secondary GB dislocations) within the perfect 9R sequence.

This is the first time the 9R structure is reported in nc Pd. This observation is unexpected when considering the high stacking fault energy (SFE) of Pd. This observation is explained by the influence of the hydrogen on the SFE of Pd and the high compressive stresses building up during hydriding.

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