Microstructure Analysis of ALD Bi_2Te_3/Sb_2Te_3 Thermoelectric Nanolaminates

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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 Bi_2Te_3/ Sb_2Te_3 superlattice nanolaminate structures 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 nanolaminate structures of alternating Bi_2Te_3 and Sb_2Te_3 ALD layers. Trimethylsilyl telluride ($(Me_3Si)_2Te$), bismuth trichloride ($BiCl_3$) and antimony trichloride ($SbCl_3$) 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 as depicted in Fig.1. 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.

This study investigates the fabrication of nanolaminates consisting of alternating semiconducting Bi_2Te_3 and Sb_2Te_3 thin films synthesized by ALD processes. The physical and structural properties of the ALD samples will be discussed in detail. The crystal structure of thin ALD telluride films was investigated by X-ray diffraction (XRD). The film morphology was inspected using a field emission scanning electron microscopy (FE-SEM) (Fig.1) and atomic force microscopy (AFM). The composition and stoichiometry were analyzed by energy dispersive X-ray spectroscopy analysis (EDS) seen in Fig. 2 and X-ray photoelectron spectroscopy (XPS). Transmission electron microscopic (TEM) studies (FEI Titan80-300) were performed to analyze the ALD deposited nanolaminate material. Cross-sectional analysis of these materials confirmed localized epitaxial like growth within individual islands, because of the similar lattice constants between the Bi_2Te_3 and Sb_2Te_3 ALD layers as demonstrated in Fig 3.

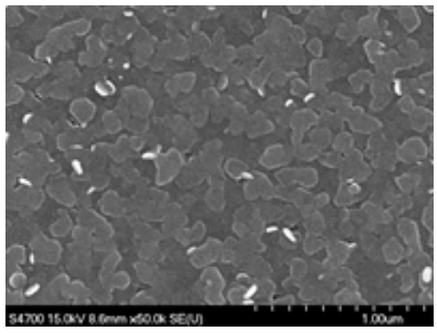

Figure 1: FE-SEM micrograph depicting the surface morphology of a Bi_2Te_3 thin film deposited with 1000 ALD cycles on silicon

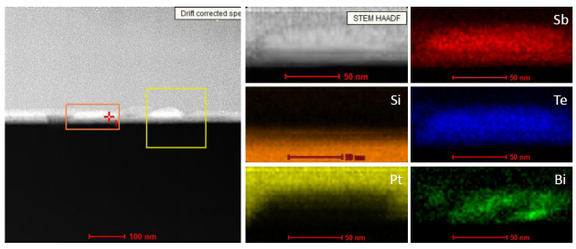

Figure 2: Energy dispersive X-ray spectroscopy (EDS) analysis identifying the constituents Sb, Bi and Te of the ALD films.

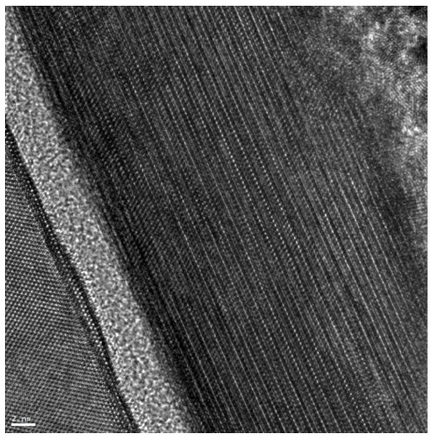

Figure 3: Nanolaminate structure of alternating ALD Bi_2Te_3 and Sb_2Te_3 layers exhibiting localized epitaxial growth as revealed by high resolution TEM X-section analysis. The alternating telluride films grow localized in graphene like fashion in hexagonal layers.