

## ALD Growth of PbTe and PbSe Superlattices for Thermoelectric Applications

Kai Zhang<sup>1,2</sup>, Arun Deepak Ramalingom Pillai<sup>1,2</sup>, David Nminibapie<sup>1,2</sup>, Madhavi Tangirala<sup>1,2</sup>, Venkata Sai Kiran Chakravadhanula<sup>3,4,5</sup>, Christian Kübel<sup>3,5</sup>, Helmut Baumgart<sup>1,2</sup>, Vladimir Kochergin<sup>6</sup>

<sup>1</sup> Department of Electrical and Computer Engineering  
Old Dominion University, Norfolk, Virginia 23529

<sup>2</sup> Applied Research Center, Newport News, Virginia

<sup>3</sup> Karlsruhe Nano Micro Facility, Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, Germany

<sup>4</sup> Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Albert-Einstein-Allee 11, 89081 Ulm, Germany

<sup>5</sup> Institute for Nanotechnology (INT), Karlsruhe Institute of Technology (KIT) - Campus Nord, Hermann-von-Helmholtz-Platz 1, Building 640, D-76344 Eggenstein-Leopoldshafen, Germany

<sup>6</sup> MicroXact Inc., 295 Industrial Drive, Christiansburg, Virginia 24073, USA

Lead chalcogenides, such as PbTe, PbS and PbSe, have attracted considerable attention because of their potential applications in thermoelectric and infrared devices. Among these materials, PbTe is an important thermoelectric material used at the intermediate temperature range of 350 - 600K due to its high figure of merit, good chemical stability, low vapor pressure and high melting point (~900 K) [1,2]. In this paper we report on the growth of alternating PbTe and PbSe films to synthesize nanolaminates on silicon substrates covered with native oxide by atomic layer deposition (ALD) for thermoelectric applications. For the synthesis of PbTe films lead bis(2,2,6,6-tetramethyl-3,5-heptanedionato) ( $\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ ) was used as chemical ALD precursor for lead and (trimethylsilyl) telluride ( $(\text{Me}_3\text{Si})_2\text{Te}$ ) for telluride. The ALD chemical precursors used for the alternate PbSe films are lead bis(2,2,6,6-tetramethyl-3,5-heptanedionato) ( $\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$ ) for lead and Bis(trimethylsilyl) selenide for Se.

In order to determine the ALD process window the influence of ALD synthesis parameters, such as substrate temperature, precursor vapor temperature, and ALD pulse time length, alternative precursor order on the microstructure and electric properties were systematically investigated. The crystal structure of thin ALD nanostructures of PbTe was analyzed by X-ray diffraction (XRD) as seen in Fig.1. The morphology was determined by field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). An example is shown in Fig. 2. The analysis of the composition and stoichiometry was carried out by energy dispersive X-ray spectroscopy analysis (EDS) and X-ray photoelectron spectroscopy (XPS) as demonstrated in Fig. 3 (a) and (b). The XRD and FE-SEM results reveal that the Lead telluride nanostructures are polycrystalline at deposition temperatures between 160 – 230 °C based on Volmer Weber Island growth mode and have characteristic FCC rock-salt crystal structure as shown in the XRD plot of Figure 2. The process window for PbSe is somewhat narrower in the range of 150 -190°C.

In addition, cross-sectional transmission electron microscopic (TEM) studies (FEI Titan80-300) performed to analyze the ALD deposited nanostructured material shall also be presented.

In this study we report on the fabrication of superlattices composed of alternating PbTe and PbSe thin films

synthesized by ALD processes for thermoelectric device fabrication.

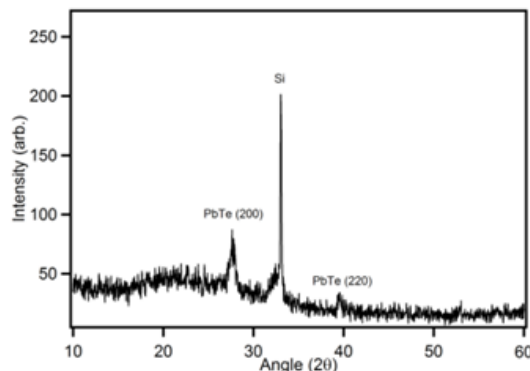


Figure 1. X-ray diffraction of ALD synthesized PbTe film.

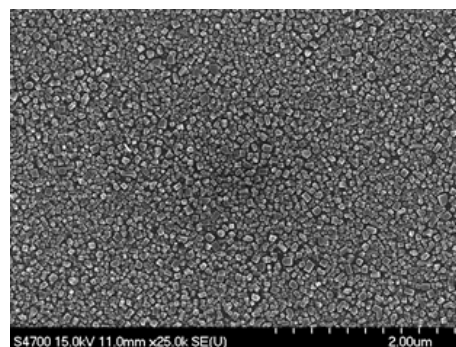


Figure 2. FE-SEM image of surface morphology of a PbTe thin film deposited with 1000 ALD cycles on silicon covered with native oxide at 180 °C.

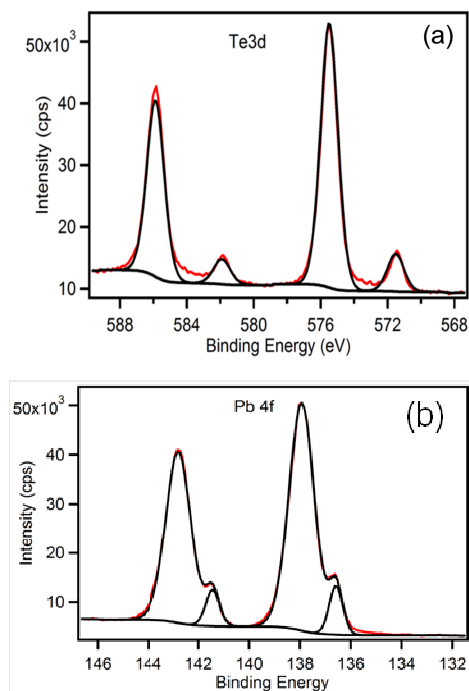


Figure 3: XPS spectra of ALD PbTe thin films: (a) Te 3d; (b) Pb 4f.

### References:

1. Heini Saloniemi, Tapio Kanninen<sup>1</sup>, Mikko Ritala, Markku Leskela, Thin Solid Films 326 78–82 (1998).
2. D.M. Freik, R.I.Zapukhlyak, M.A. Lopjanka, G.D. Mateik, R.Ya. Mikhajlonka, Semiconductor Physics, Quantum Electronics & Optoelectronics, Vol. 2, N 3, 62-65 (1999).