

## Materials Characterization of Thin Films Printed with Ge<sub>20</sub>Se<sub>80</sub> Ink

Al-Amin Ahmed Simon<sup>1\*</sup>, Shah Mohammad Rahmot Ullah<sup>1</sup>, Bahareh Badamchi<sup>1</sup>, Harish Subbaraman<sup>1</sup> and Maria Mitkova<sup>1</sup>

<sup>1</sup> Department of Electrical and Computer Engineering/Boise State University, Boise, USA.

\* Corresponding author: alaminahmedsimon@u.boisestate.edu

Additive manufacturing or 3D printing has been of vital importance in recent years due to its several advantages over traditional manufacturing technologies (e.g. Low cost, High throughput, High conformity). Printing has the potential to fabricate a device on non-flat surfaces and for sensing application this is an important advantage. This enables direct contact measurement of various physical parameters by fabricating the device directly on the surface to be monitored. Ink formation, printing and sintering are three major steps in additive manufacturing. Depending on the printing technology like inkjet, aerojet or syringe dispensing systems, inks of different parameters (e.g. particle size, viscosity, surface tension) are produced. Printing step is optimized for the specific equipment and sintering depends on the ink material, application requirement etc.

This paper reports progress in developing additive manufacturing of radiation hard temperature sensor that can measure 650K-800K. The structure of the sensors involves a layer of chalcogenide glass that undergoes phase change and becomes crystalline at a certain temperature. This changes the optical and electrical properties of the material. The goal is to utilize the change in optical properties with a waveguide and the change in electrical performance as a measurement of the temperature. The working principle has been proved by simulation and in thermally evaporated films [1,2]. To apply additive manufacturing for device fabrication, we have developed chalcogenide glass nanoparticle ( $\leq 100$  nm diameter) ink from 5N pure elements by glass synthesis, wet milling, ultrasonication then centrifugation and have been able to obtain printed films using an inkjet printer. There are some recent data about room temperature printing of silica glass to obtain films with bulk like properties [3]. The crucial step of sintering requires special attention as slight over or under heating could cause cracks and change the transmission spectra of the glass. Data about sintering of chalcogenide glass ink, based on Ge-Se glasses are not available and, in this regard, this is a novel approach to produce chalcogenide glass thin films. The goal is to produce amorphous film with bulk like composition and low surface roughness. The quality of such films has been characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Atomic Force Microscopy (AFM).

Here, results related to Ge<sub>20</sub>Se<sub>80</sub> printed films are reported. The amorphous nature of the printed films is confirmed by XRD data (Fig 1). A trace of crystalline Fe<sub>2</sub>O<sub>3</sub> is found in the thin film, which can be attributed to mixing of milling ball residue. Due to the high concentration of defects in amorphous Ge<sub>20</sub>Se<sub>80</sub>, it has a relatively high tolerance for impurities. So, it is expected that the iron oxide will not affect the thin film properties. EDS was done to confirm the composition of the film (Fig. 2a), which shows that the compositional variance of the thin film is within  $\pm 1\%$  when compared to the composition of the bulk glass, from which the ink has been obtained. SEM micrographs show that the unsintered films have separated particles (Fig. 2b). These particles give rise to surface roughness and scatter any light incident upon it. Annealing can be done to sinter the printed films and after careful consideration of the ink components we have established a sintering process. First the films were heated at 353K for 5 days and then the films were heated at 723K for 15min. One important parameter referring to the effects of annealing could be surface roughness. So, AFM images were taken to obtain surface morphology

(Fig. 3a). It is particularly effective in analyzing surface roughness of the printed films. From the AFM data, it is evident that the surface roughness reduces after annealing (Fig. 3b).

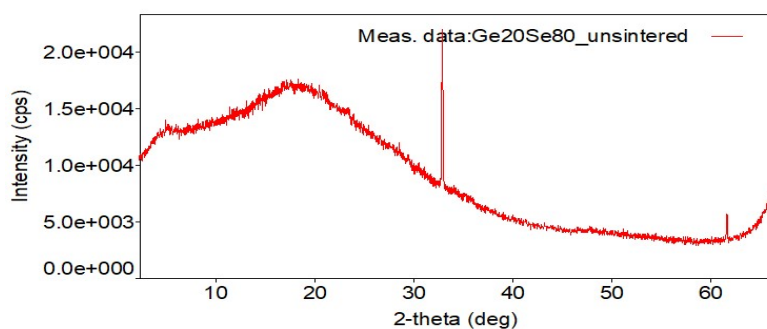
Analysis of characterization data suggests that the developed sintering process produces continuous thin film. The used characterization methods are critical for understanding the optimization process for production of high-quality inks and films.

#### Reference:

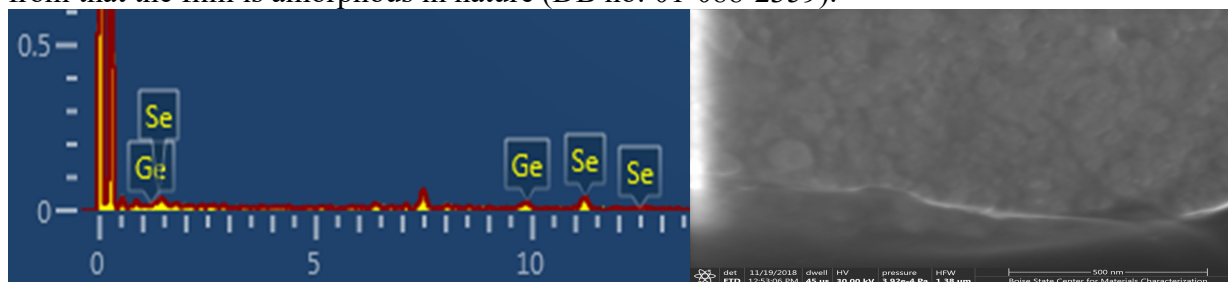
[1] A Ahmed Simon et al., NPIC & HMIT (2019) in press.

[2] B Badamchi et al., NPIC & HMIT (2019) in press.

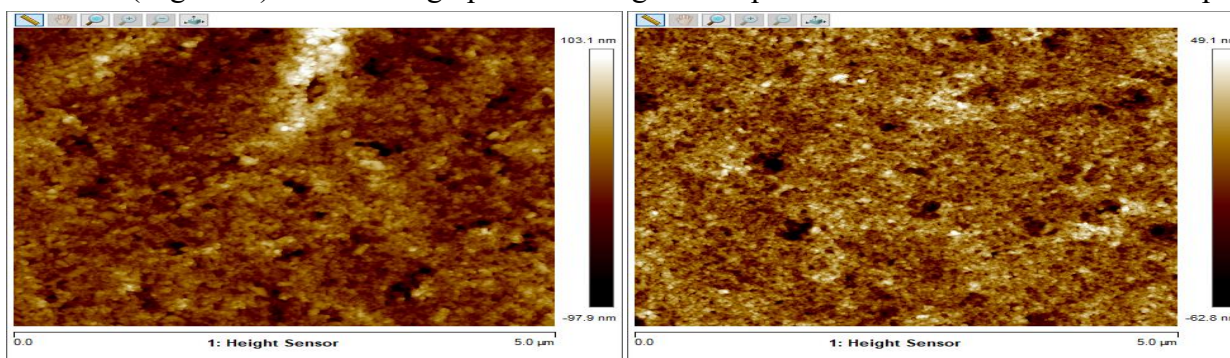
[3] F Kotz et al., Nature **544** (2017), p. 337.



**Figure 1.** XRD plot of the printed  $\text{Ge}_{20}\text{Se}_{80}$  film. The plot indicates a trace of  $\text{Fe}_2\text{O}_3$  in the film apart from that the film is amorphous in nature (DB no: 01-088-2359).



**Figure 2.** (Left: 2a) EDS spectra of  $\text{Ge}_{20}\text{Se}_{80}$  printed film shows that the composition is within  $\pm 1\%$  of the bulk. (Right: 2b) SEM micrograph on one edge of the printed film shows unsintered nanoparticles.



**Figure 3.**  $\text{Ge}_{20}\text{Se}_{80}$  printed films (Left: 3a Unsintered film, roughness 24nm) (Right: 3b Thermally Sintered at  $450^\circ\text{C}$  for 15min, roughness 14.3nm). This also confirms that the particle size is around 100nm. (Courtesy of Surface Science Laboratory, Boise State University)