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Thermal Annealing Effects on the Thermoelectric and Optical Properties of SiO_2/SiO_2+Au Multilayer Thin Films

S. Budak*, S. Yang, Z. Xiao, R. B. Johnson

Department of Electrical Engineering & Computer Science, Alabama A&M University, Normal, AL USA

Abstract Thermoelectric thin films have been prepared from 100 alternating layers of SiO_2/SiO_2+Au superlattice films using Magnetron DC/RF Sputtering. Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) have been used to analyze the surface and composition of the thin films. In order to form nano-structures (nano-dots and/or nano-clusters) in the multilayers, the fabricated thin films were annealed at different temperatures ranging between 100°C and 400°C. The thin films annealed at different temperatures have been characterized using Seebeck coefficient measurement, van der Pauw resistivity measurement, mobility, density, Hall Effect measurements, Optical absorption spectroscopy, SEM and EDS analysis, and Atomic Force Microscopy (AFM). The Seebeck coefficient reached its highest value for the sample annealed at 500°C when the measurement temperature reached 360 K. The highest Seebeck coefficient was recorded as about -425 μV/K at 360 K. The resistivity values increased when it was annealed at 100°C, and then decreased and reached the lowest value when the annealing temperature reached the 200°C. Temperature annealing affected the negative mobility and Hall Effect coefficients to shift to the positive direction. The optical absorption spectra got narrower when the annealing temperatures increased. SEM shows that the surface of the multilayer thin films is very smooth.

Keywords Thermal annealing, Thermoelectric and optical properties, Multi-Nanolayers, Figure of merit

1. Introduction

Thermoelectric materials are increasingly becoming more important due to their applications in thermoelectric power generation as heat harvesting and microelectronic cooling devices [1, 2]. The theory of thermoelectric power generation and thermoelectric refrigeration was first presented by Altenkirch in 1990 [3]. The efficiency of the thermoelectric devices and materials is determined by the figure of merit [4] $ZT = S^2\sigma T / \kappa$ where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ is the thermal conductivity [5, 6]. Effective thermoelectric materials and devices have a low thermal conductivity and a high electrical conductivity [7]. Solid state thermoelectric devices are reliable energy converters since they do not have noise or vibration due to not having mechanical moving parts [8]. Therefore, thermoelectric materials (TEM) are attracting worldwide attention now, for use of exhaust waste heat from power plant or automobile [9]. Recent years witnessed remarkable growing interest in thermoelectric nano-composite for energy conversion applications [10]. Our previous studies on the similar multilayer thin films are given in ref. [1, 11-15]. In this study we report on the preparation of the thermoelectric thin films with the 100 alternating SiO_2/SiO_2+Au nano-layers, thermal annealing effects on the fabricated thermoelectric thin film systems and their characterizations with Seebeck coefficient measurement, van der Pauw resistivity measurement, mobility, density, Hall Effect measurements, Optical absorption spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis, and Atomic Force Microscopy (AFM).

2. Experimental

We have deposited the thin films with 100 alternating SiO_2/SiO_2+Au nano-layers on silicon (Si) and fused silica (suprasil) substrates by magnetron DC/RF sputtering as shown in figure 1. The multilayer thin films were sequentially deposited to have a periodic structure consisting of alternating SiO_2 and SiO_2+Au layers. These thin films form a periodic quantum well structure consisting of 100 alternating layers of total thickness of 1211 nm. The DC (Direct Current) gun was used to sputter Au material while RF (Radio Frequency) gun was used to sputter SiO_2. Ar gas was used to form plasma in the DC/RF sputtering chamber during the deposition. The chamber was pumped down to about $5x10^{-5}$ Torr. The deposition was performed when the pressure was about $3x10^{-3}$ Torr. The substrates were mounted on the substrate holder and rotated during the whole deposition process. The growth rate was monitored by an

* Corresponding author:
satilmis.budak@aamu.edu (S. Budak)
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INFICON Quartz Crystal Microbalance (QCM). In order to form nano-structures (nano-dots and / or nano-clusters) in the multilayers, the fabricated thin films were annealed at different temperatures ranging between 100°C and 400°C. The thin films annealed at different temperatures have been characterized using Seebeck coefficient measurement, van der Pauw resistivity measurement, mobility, density, Hall Effect measurements, Optical absorption spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis, and Atomic Force Microscopy (AFM).

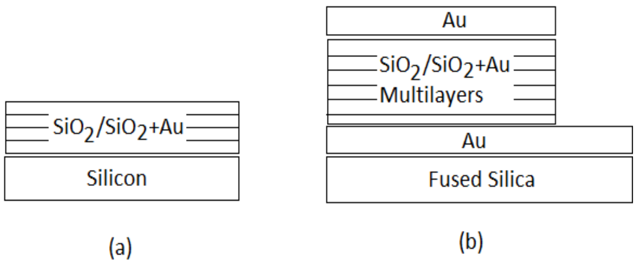

Figure 1. Cross Sectional Deposition Geometry of 100 alternating SiO_2/SiO_2+Au nano-layers on (a) silicon (Si) and (b) fused silica (suprasil) substrate

3. Results and Discussion

Figure 1 shows the cross-sectional deposition geometry of 100 alternating SiO_2/SiO_2+Au nano-layers on (a) silicon (Si) and (b) fused silica (suprasil) substrate. The sample geometry given in figure 1(a) is for van der Pauw, SEM, and optical measurements; 1(b) is for Seebeck coefficient measurements.

Figure 2 shows the temperature dependence of Seebeck coefficients of 100 multilayers of SiO_2/SiO_2+Au thin films annealed at the different temperatures. As seen from figure 2, the Seebeck coefficient increased in the negative direction when they were annealed at suitable temperatures. When the annealed samples were measured for their Seebeck coefficient depending on temperatures change, the increase in Seebeck coefficient in negative direction was recorded for the samples annealed at 400°C and 500°C. The Seebeck coefficient reached its highest value for the sample annealed at 500°C when the measured temperature reached 360 K. As seen from figure 2, the highest Seebeck coefficient was recorded as about -425 µV/K at 360 K. The increase in Seebeck coefficient is one of the expected parameters for the high efficient thermoelectric materials and devices. We did similar studies on the same multilayer systems before and, we reached the Seebeck coefficient of about -60 µV/K at 360 K for 50 multilayers at the thickness of 500 nm [1], and the Seebeck coefficient of about -50 µV/K at 360 K for 50 multilayers at the thickness of 147 nm [14]. Our reaching here the much higher Seebeck coefficient might arise from a) the number of multilayers was doubled, and b) the total thickness of the multilayer thin films was higher than the doubles of the sample in ref. [1] and eight times thicker than the sample in ref. [14]. The previous two studies have been modified to form nano-clusters and/or nano-dots in the multilayers using high-energy ion bombardment, but the current study has been performed under the different temperatures for annealing to form nano-dots and/or nano-clusters in the multilayers. It seems that the chosen annealing temperatures and the films thickness for the current study have better effects on the multilayer thin film systems than the high energy beam at the previous selected fluences. Both temperature annealing and ion beam bombardment cause the similar effects on the Seebeck coefficient of the multilayered thin film systems.

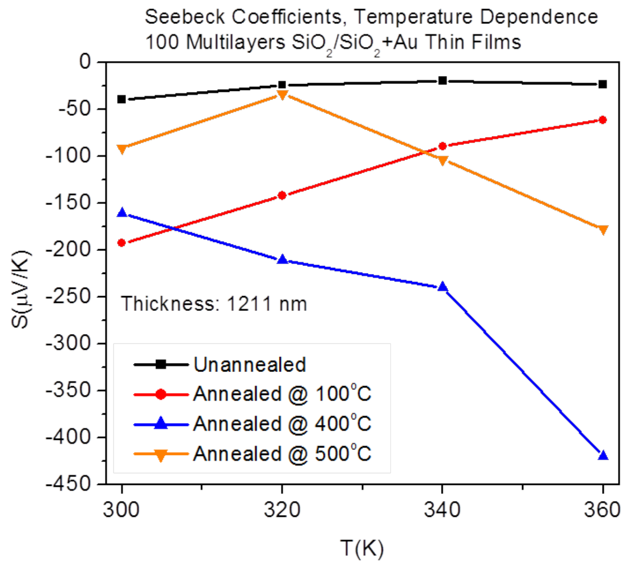

Figure 2. Temperature Dependence of Seebeck Coefficients of 100 Multilayers of SiO_2/SiO_2+Au Thin Films Annealed at the Different Temperatures

Figure 3 shows the annealing temperature dependence of Seebeck coefficients measured at room temperature of 100 multilayers of SiO_2/SiO_2+Au thin films. This result could be seen easily from figure 2 if one could look at the room temperature measurement (300 K). As seen from figure 3, the sample annealed at 100°C reached the highest value of about -190 µV/K. Similar graphs could be redrawn using the Seebeck coefficient values at 320 K, 340 K and 360 K. As seen from figure 2, the highest Seebeck coefficient reached the value of about -425 µV/K at 360 K as mentioned in the previous figure.

Figure 4 shows the temperature dependence of van der Pauw resistivity values of 100 multilayers of SiO_2/SiO_2+Au thin films annealed at the different temperatures. As seen from figure 4, the resistivity values increased when it was annealed at 100°C, and then decreased and reached the lowest value when the annealing temperature reached the 200°C. It seems that the annealing has positive effects on the increment of the electrical conductivity. The increase in the electrical conductivity is one of the other important parameters among the thermoelectrical properties. We have seen similar increments in the electrical conductivity measurements for the sample given in fences [1, 14] for the

50 multilayers of the same systems at the different thickness and under high beam modification. As we have seen from the graph in figure 4, the thermal annealing brought positive effects on the electrical conductivity values.

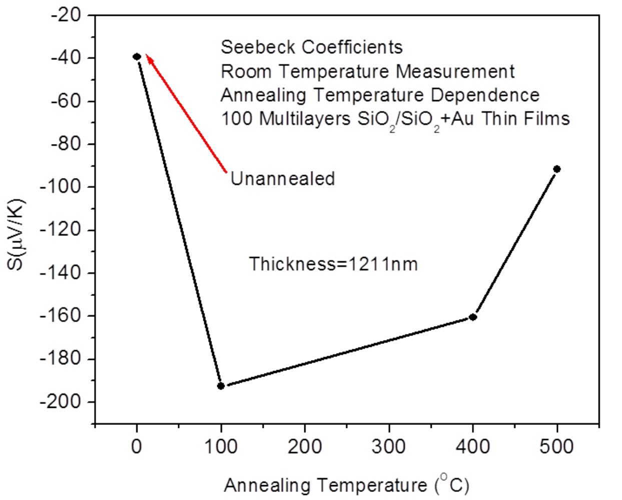

Figure 3. Annealing Temperature Dependence of Seebeck Coefficients Measured at Room Temperature of 100 Multilayers of SiO_2/SiO_2+Au Thin Films

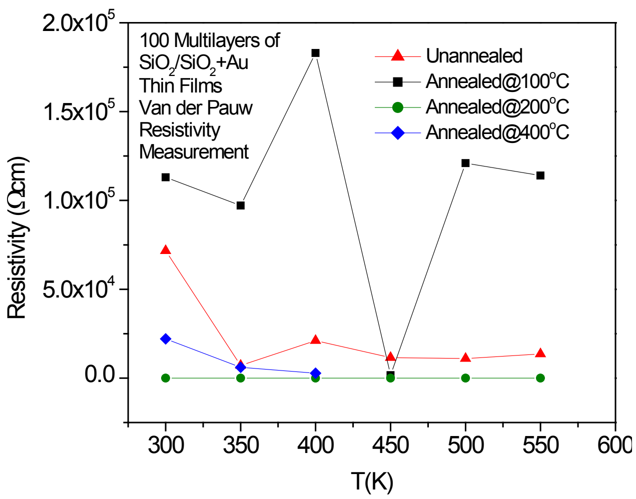

Figure 4. Temperature Dependence of van der Pauw Resistivity Values of 100 Multilayers of SiO_2/SiO_2+Au Thin Films Annealed at the Different Temperatures

Figure 5 shows the temperature dependence of mobility values of 100 multilayers of SiO_2/SiO_2+Au thin films annealed at the different temperatures. From figure, annealing affected the negative mobility to shift to the positive direction. It might give some idea of the releasing positive charge carriers from the multilayers structures due to the annealing and contributing to the transport properties.

Figure 6 shows the temperature dependence of Density values of 100 multilayers of SiO_2/SiO_2+Au thin films annealed at the different temperatures. As seen from the figure, annealing has the similar effects on the density like on the effect on the mobility. The density started to shift to low values after annealing was introduced like 100°C and 400°C.

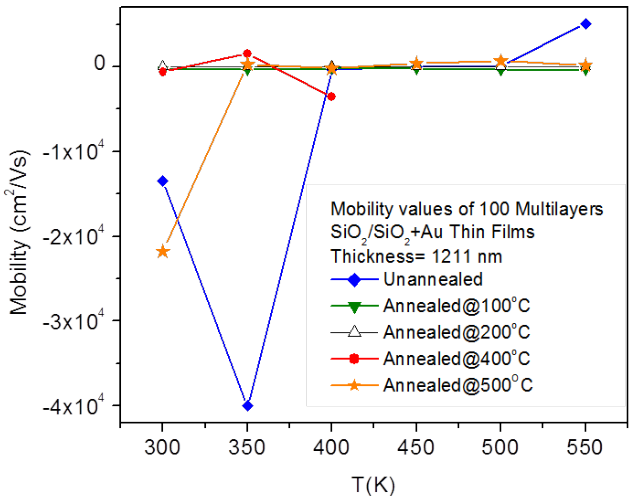

Figure 5. Temperature Dependence of Mobility Values of 100 Multilayers of SiO_2/SiO_2+Au Thin Films Annealed at the Different Temperatures

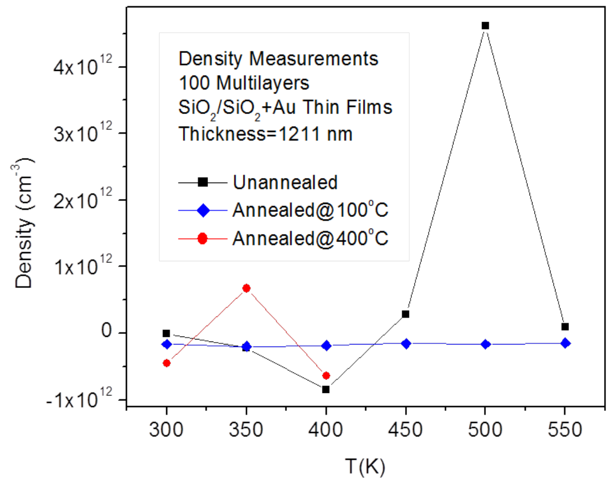

Figure 6. Temperature Dependence of Density Values of 100 Multilayers of SiO_2/SiO_2+Au Thin Films Annealed at the Different Temperatures

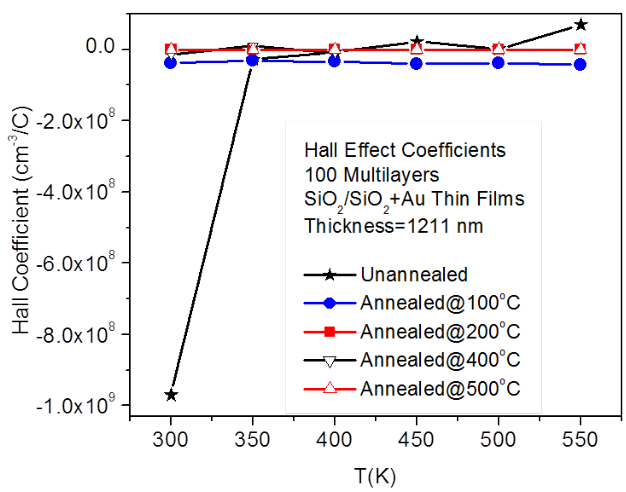

Figure 7. Temperature Dependence of Hall Coefficients of 100 Multilayers of SiO_2/SiO_2+Au Thin Films Annealed at the Different Temperatures

Figure 7 shows the temperature dependence of Hall coefficients of 100 multilayers of SiO_2/SiO_2+Au thin films annealed at the different temperatures. As seen from the figure, annealing affected the negative Hall Effect coefficients to shift to the positive direction. Annealing has similar effects on the Hall Effect coefficient like it does on mobility. Since the Hall Effect is related to mobility and density of the charge carriers, the behavior resembles to the mobility. The more detailed temperature on the similar system under the different magnetic field for the Hall Effect measurements has been planned.

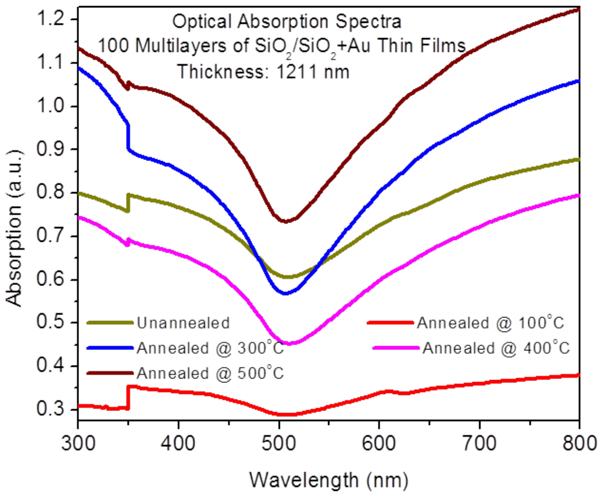

Figure 8. Optical Absorption Spectra of 100 Multilayers of SiO_2/SiO_2+Au Thin Films Annealed at the Different Temperatures

Figure 8 shows the optical absorption spectra of 100 multilayers of SiO_2/SiO_2+Au thin films annealed at the different temperatures. As seen from the figure, the optical absorption spectra are getting narrower when the annealing temperatures increased. The optical absorption is a sign of the nanodots formation in the multilayers. It has been planned to work with these systems to find the average nano-dots size using Mie's theory and Doyle's [16] formula. We did some preliminary study on the optical absorption of Au nano-crystal formation in silica [11]. Metallic ion implantation and thermal annealing result in metal nano-clusters to precipitate and change the linear and nonlinear optical properties near the surface of the silica glass. Implantation at elevated temperatures or at fluences above a threshold, causes spontaneous nano-cluster formation without additional thermal treatment. The average radius r of the metallic clusters can be calculated according to Doyle formula from the absorption spectra using the equation

$$r = \frac{v_f}{\Delta w_{1/2}} \tag{1}$$

Where v_f : electron velocity corresponding to the Fermi energy of the metal (v_f =1.39×10^8 cm s^{-1} for gold) and $\Delta w_{1/2} = 2\pi c(\Delta\lambda / \lambda_p^2)$, where $\Delta\lambda$ is the full width at half maximum (FWHM) wavelength and λ_p is the peak wavelength both determined from an optical absorption spectrum. λ_p depends on the element implanted and $\Delta\lambda$ is related to the size of the nano-clusters [11].

Figure 9 shows the Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis of unannealed 100 multilayers of SiO_2/SiO_2+Au thin film. SEM shows that the surface of the multilayer thin films is very smooth. The EDS shows the quantitative analysis as seen from figure 9.

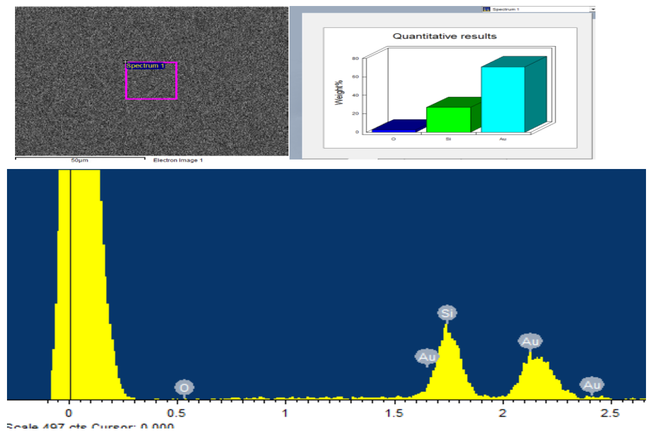

Figure 9. SEM+EDS Analysis of Unannealed 100 Multilayers of SiO_2/SiO_2+Au Thin Film

Figure 10 shows the SEM mapping analysis of unannealed 100 multilayers of SiO_2/SiO_2+Au thin film. The SEM mapping results as shown in figure 10, each element has its own mapping and combination of all mapping gives us the SEM micrograph of the fabricated thermoelectric thin films.

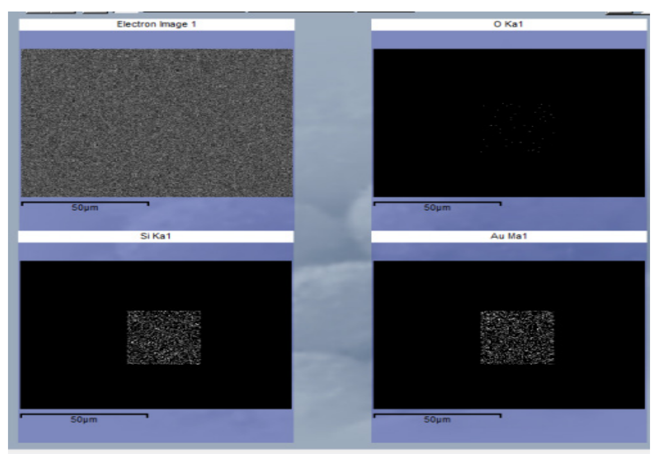

Figure 10. SEM Mapping Analysis of Unannealed 100 Multilayers of SiO_2/SiO_2+Au Thin Film

Figure 11 shows AFM images of 100 multilayers of SiO_2/SiO_2+Au thin films for unannealed and annealed at 100°C. As seen from the figure 11, annealing at 100°C did not show too much change on the surface of the thin films.

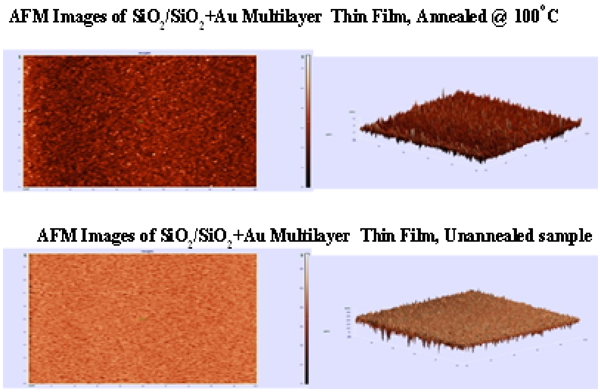

Figure 11. AFM Images of 100 Multilayers of SiO_2/SiO_2+Au Thin Films for Unannealed and Annealed at 100°C

4. Conclusions

In this study we reported on the preparation of the thermoelectric thin films with the 100 alternating SiO_2/SiO_2+Au nano-layers, thermal annealing effects on the fabricated thermoelectric thin film systems and their characterizations with Seebeck coefficient measurement, van der Pauw resistivity measurement, mobility, density, Hall Effect measurements, Optical absorption spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) analysis, and Atomic Force Microscopy (AFM). The Seebeck coefficient reached its highest value for the sample annealed at 500°C when the measured temperature reached 360 K. The highest Seebeck coefficient was recorded as about -425 µV/K at 360 K. The resistivity values increased when it was annealed at 100°C, and then decreased and reached the lowest value when the annealing temperature reached the 200°C. Temperature annealing affected the negative mobility and Hall Effect coefficients to shift to the positive direction. The optical absorption spectra got narrower when the annealing temperatures increased. SEM shows that the surface of the multilayer thin films is very smooth. We are planning more detailed temperature range for the characterizations to see more effective and accurate results.

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