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Investigation of large Seebeck effect by charge mobility engineering in $CuAlO_2$ thin films grown on Si substrate by thermal evaporation

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ABSTRACT

In this research paper, we have reported giant enhancement in Seebeck coefficient of $AlCuO_2$ thin films by charge mobility engineering. Thin films of $AlCuO_2$ were grown by the evaporation of Al and Cu powder in tube furnace on Si (100) substrate. The experimental conditions were sets as; tube pressure (0.2 Torr), source to substrate distance (3 cm), evaporation temperature (1000 °C), oxygen flow rate (60 sccm) and evaporation time was (30 min). The charge mobility and diffusion of oxygen atoms were controlled by annealing the grown samples in oxygen environment at various temperatures from 600 to 800 °C with a step of 100 °C for one hour in muffle furnace. The observed giant enhancement in Seebeck coefficient (150–1050 μV/K) can be explained as; The annealing generates oxygen interstitials and causes the charge scattering mechanism shift from lattice to impurity scattering mechanism. In the impurity scattering mechanism, mobility of charge carriers increased with temperature. This increase in mobility results in the giant enhancement of Seebeck coefficient. The argument was verified by Hall data which suggested that concentration of oxygen interstitials increased by annealing temperature. To further strengthened our argument we have performed XRD and FTIR measurements. XRD data has showed that as grown sample consists of one peak at angle 32° related to (006) phase of $CuAlO_2$. Annealing resulted in the generation of new phases at angles 35°, 42.5° and 48.4° which were related to CuO (111), $CuAlO_2$ (104) and $CuAlO_2$ (009) respectively. FTIR spectrum verified the presence of Cu-O and Al-O at wavenumbers 450 cm^{-1} and 600 cm^{-1} respectively.

1. Introduction

Conventional energy sources such as oil and gas are causing threat for environment due to production of carbon dioxide in the air. Therefore, renewable energy sources like photovoltaic, fuel cells, wind, nuclear and thermoelectric are gaining interest of research community [1–5]. Thermoelectric power generation (direct conversion of heat into useful energy) is supposed to be powerful source of renewable energy because it uses waste heat for energy conversion [6]. It also has some other advantages such as noise and maintenance free, cheap electricity, no moving parts, when compared with its counterparts [7–9]. The performance of any thermoelectric material can be judged by dimensionless quantity figure of merit define by following formula

$$ZT = S^2 \ \sigma / \kappa$$

Where S is Seebeck coefficient, σ is electrical conductivity and κ is thermal conductivity [10].

Therefore, materials with large Seebeck coefficient, high electrical conductivity and low thermal conductivity are highly desirable [11]. Various strategies such as new compound development, optimization of carrier concentration and nano-structuring were employed to enhance the thermoelectric properties. The conversion efficiency of popular thermoelectric materials (Bi_2Te_3, PbTe and SiGe) have been reported only 5–10% causing the value of ZT is still inadequate for widespread applications [12,13]. Recently, a new method was reported in nature communications by Sun et al. to enhance the Seebeck coefficient by charge mobility engineering in Ni-doped $CoSb_3$ [14]. P-type $CuAlO_2$ semiconductor alloy with moderate band gap of 1.9 eV has a property to modulate its charge carrier concentration and mobility by thermal annealing, therefore emerging as potential thermoelectric material. Furthermore, this p-type thermoelectric material has some remarkable properties such as chemical and thermal stability at high temperatures, abundant, cheap growth, nano-structuring and microstructure control by thermal annealing. On the other hand, annealing in oxygen environment is powerful way to modulate the microstructure and hence we can control the thermoelectric properties. We are first to report such giant Seebeck coefficient in $CuAlO_2$ using charge mobility engineering concept reported by Sun et al. according to best of our knowledge.

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In this paper, we have reported high Seebeck coefficient of 1050 μV/K in $CuAlO_2$ grown on Si substrate by the evaporation Cu and Al in tube furnace. The grown sample was cut into pieces and annealed in oxygen environment at various temperatures from 500 to 800 °C to modulate the charge mobility and density of oxygen interstitials intrinsic defects. XRD and FTIR measurements confirmed the formation of oxygen interstitials types defects in annealed $CuAlO_2$.

2. Experimental

Copper and Aluminum metal powders with purity 99.99% were obtained from Sigma h Aldrich labs. By mixing and crushing using mortar and pestle, pallets of different concentration of Cu and Al were prepared with the help of hydraulic press apparatus at specific pressure of 12–13 t. Pallets were then evaporated and deposited on silicon substrate using followings experimental conditions; tube pressure (0.2 Torr), source to substrate distance (3 cm), evaporation temperature (1000 °C), oxygen flow rate (60 sccm) and evaporation time was (30 min). After growth, a representative sample was cut into pieces and annealed in oxygen environment at various temperatures from 600 to 800 °C with step of 100 °C for one hour.

The structural characterization of grown thin films was performed by X-Ray Diffraction (Bruker D8) having Cuk_{α} source with wavelength 1.54 Å. The chemical bonding was verified by Fourier Transform Infrared Spectroscopy (Perkin), the seebeck coefficient was measured using home made Seebeck system and four point probe for conductivity measurements.

3. Results and discussion

Fig. 1 represents the XRD pattern of as grown and annealed $CuAlO_2$ deposited on silicon substrate in a tube furnace at evaporation temperature 1000 °C. The un-annealed sample consists of one major phase at 2θ = 32.05 which belongs to $CuAlO_2$ (006) plane [15]. Annealing resulted in development of new phases at 2θ = 35.4, 42.4, 46.2, 48.4, 57.3 and 58.7 related to CuO (1 1 1), and $CuAlO_2$ (1 0 4), (0 0 9), (0 1 5) (0 1 8) and (2 0 2) orientations respectively [16–19]. The preferred orientation is along (0 0 6) because it shows maximum intensity. This phenomena is attributed that the formation of $CuAlO_2$ phase is sensitive to oxygen density [20]. As the annealing temperature increases, the intensity of oxygen sensitive (006) plane is increased which confirmed that density of oxygen atoms in the crystal increases with annealing temperature.

The structure of grown thin films was also verified by FTIR data (not shown here). We have observed a prominent peak at 463 cm^{-1} which is due to Cu-O stretching vibrations. Whereas some small peaks ranging between 495 cm^{-1} to 550 cm^{-1} were also observed and are related to Cu-O stretching vibrations as described Azam et al. [21]. The small peak at 600 cm^{-1} is related to Al-O short vibrations in AlO_6 octahedral.

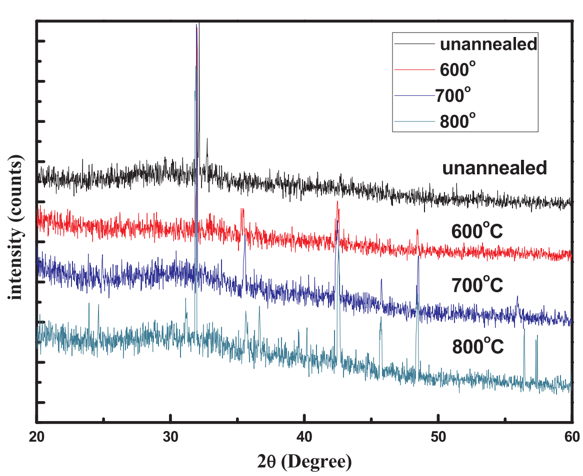

Fig. 1. XRD pattern of as grown and annealed $CuAlO_2$ at various temperatures from 600 to 800 °C for one hour. The data confirmed that intensity of oxygen sensitive 006 plane increases with annealing temperature.

Fig. 2(a, b, c and d) shows variation in induced emf as a function of temperature difference created between two ends of un-annealed and annealed samples at room temperature, 100 °C, 150 °C and 200 °C. It is clear from the graphs that for each sample the value of induced emf is increasing with an increase in temperature difference. It is also noted that annealed as well as samples with high measurement temperature show higher induced voltage as compared to un-annealed. It is pertinent to mention here that no contribution in induced voltage from the Si substrate is expected because there is barrier between n-type Si and p-type $CuAlO_2$ thin films. The values of Seebeck coefficient were calculated for all samples from the slopes of straight lines using these graphs and are plotted in Fig. 3.

Fig. 3 represents the Seebeck coefficient as a function of annealing temperature at various measurement temperatures. The value of Seebeck coefficient is increasing with increase in annealing temperature. It is also observed that annealed samples also obeyed the increasing trend in Seebeck coefficient with increasing measurement temperature from 50 to 200 °C. This may be attributed to increased mobility of carrier at high measurement and annealing temperatures. In general, there are two contributions to Seebeck coefficient namely diffusion and phonon drag [22]. As temperature (both annealing and measurement temperatures) increases, the diffusion rate of oxygen atoms to interstitials sites in the lattices is also increased, therefore increase in Seebeck coefficient is expected. Furthermore, high temperature annealing generates intrinsic defects in grown samples so the scattering mechanism shifts from lattice to impurity scattering mechanism. In the impurity scattering mechanism, mobility of carriers increases with temperature, again verifying the increase in Seebeck coefficient. The mobility enhancement in Seebeck coefficient was also investigated by Sun et al. in Ni doped $CoSb_3$ system [14]. In the entire range of investigations the Seebeck coefficient is found to be positive, indicating p-type conductivity of the films due to major contribution of holes

Fig. 4 demonstrated the effect of annealing temperature on the conductivity of annealed $CuAlO_2$ thin films grown on Si substrate. It is observed that the conductivity of annealed films increases from 0.02 to 2.5 S/cm as the annealing temperature increases from 600 to 800 °C. As for as wide band gap semiconductors such as ZnO and related materials concerned, electrical conductivity is strongly dependent on the concentration of intrinsic defects. For instance, oxygen vacancies and zinc interstitials are the source of n-type conductivity in ZnO. In literature several mechanisms have been proposed for electrical conductivity enhancement in $CuAlO_2$ thin films. For example Tawat et al. proposed that Cu vacancies and Cu_{Al} antisites are supposed to be strong candidates for hole generation in $CuAlO_2$ [23]. Kawazoe et al. and Banerjee et al. [24,25] demonstrated that oxygen vacancies are the strong contributor towards the intrinsic p-type conductivity of $CuAlO_2$. Furthermore, theoretical studies also revealed that Cu vacancies and oxygen interstitials have lowest formation energies in $CuAlO_2$ crystal, therefore their formation is much probable [26,27]. The effect of intrinsic defects on the thermoelectric properties in $CuInTe_2$ is also described in the literature [28]. We argued that annealing in oxygen environment can generates O-interstitials type defects, therefore increase in the conductivity of annealed films is understandable. This increase in conductivity behavior is also verified by the XRD.

Fig. 5 depicts the effect of annealing temperature on the power factor of annealed $CuAlO_2$ thin films grown on Si substrate in tube furnace. The power factor can be described by the following formula

$$\textbf{Power factor} = S^2\alpha$$

where S is Seebeck coefficient and α is electrical conductivity. The power factor is enhanced significantly with increasing annealing and measurement temperature because both Seebeck coefficient and