The electrical, optical properties of AlSb polycrystalline thin films deposited by magnetron co-sputtering without annealing*

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In order to fabricate AlSb polycrystalline thin films without post annealing, this paper studies a technology of magnetron co-sputtering onto intentionally heated substrate. It compares the structural characteristics and electrical properties of AlSb films which are deposited at different substrate temperatures. It finds that the films prepared at a substrate temperature of 450 °C exhibit an enhanced grain growth with an average grain size of 21 nm and the lattice constant is 0.61562 nm that goes well with unstained lattice constant (0.61355 nm). The $\ln(\sigma_{\rm dark}) \sim 1/T$ curves show that the conductivity activation energy is about 0.38 eV when the film is deposited at 450 °C without an annealing. The transmittance and reflectance spectra show that the film deposited at 450 °C has an optical band gap of 1.6 eV. These results indicate that we have prepared AlSb polycrystalline films which do not need a post annealing.

Keywords: AlSb thin films, magnetron sputtering, solar cells

PACC: 7280E, 7360F, 7360L, 7865K

1. Introduction

Recently, much attention has been paid to the development of low cost, high efficiency thin film solar cells. The AlSb is an indirect band semiconductor with band-gap of about 1.62 eV at room temperature and its theoretical conversion efficiency is more than 27%.[1] Moreover, AlSb is an environment-friendly material with the reserves of both Al and Sb being very rich in the Earth. The AlSb has been chosen as one of the most promising materials for photovoltaic applications.

For fabrication of the AlSb films a variety of preparation techniques have been employed such as co-evaporation,[2,3] hot wall epitaxy.[4] The possibility of self-epitaxial growth of laser irradiated AlSb films was studied by Baufay *et al.*[5] The flash evaporation technique has been employed by Richards *et al.*[6,7] to grow AlSb films. Laroux *et al.*[8] have employed metal organic chemical vapour deposition (MOCVD) to grow AlSb films on insulating substrates. The AlSb films have also been prepared by liquid phase epitaxy (LPE)[9] and laser annealing.[10] Of the methods mentioned above, the epitaxial growth methods which are used to fabricate single crystal films have a higher preparation cost; the technique of vacuum evaporation and flash evaporation are not easy to precisely control the evaporation rate of each source, while the equipment of MOCVD is much more complicated. The magnetron sputtering method is expected to be promising for binary metal thin film preparation because metal targets can be used and the compositions of films are controllable.[11] For the preparation of AlSb, both Al and Sb target are much easier to obtain in comparison with AlSb target, which has an extremely high price. Moreover, it is much easier to control the compositions by co-sputtering in contrast to other methods because of the low melting point of Al and Sb. However, little work has been reported on the properties of AlSb thin films prepared by magnetron co-sputtering.

In our previous work, AlSb films have been fabricated by magnetron sputtering with post annealing. It was found that when the annealing temperature was around 450 °C, AlSb films exhibit well electrical and optical properties.[12] However, some unfavorable fac-

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tors may occur during the annealing process, such as the precipitation of Sb and the introduction of oxygen which would lead to oxidation of AlSb films due to its high affinity to oxygen. In order to improve the films quality and decrease the fabrication cost, we try to investigate the feasibility of preparing films without a post heat treatment. In the present paper, we have made a comparative study of the properties of AlSb films deposited at different substrate temperatures with varying annealing parameters. The electrical, structural and optical properties of the films were investigated.

2. Experimental

The AlSb thin films were deposited by magnetron sputtering system. The film was simultaneously sputtered from highly pure Al (5N) and Sb (5N) targets onto intentionally heated quartz glass. The quartz substrates were cleaned ultrasonically in acetone and de-ionized water. The diameter of the targets was 640 mm and the substrate-to-target distance was 100 mm. The deposition was carried out in an argon and hydrogen gas mixture atmosphere, with DC power of Al and Sb for 100 W and 30 W respectively. Each target was pre-sputtered for 5 minutes before each sample deposition in order to remove possible contaminations on the target surface. The deposition chamber was pre-pumped down to a base pressure of 4×10^{-4} Pa with a turbomolecular pump. The deposition pressure was fixed at 0.5 Pa throughout this work.

The x-ray diffraction spectra was acquired with a diffractometer (Dandong Fangyuan Instrument LLC, DX-2500) using Cu Ka radiation (λ = 1.5405 Å, 1 Å=0.1 nm). The scan range was 10 °C–70 °C and the velocity was 0.03°/s. The film thickness was measured by the stylus profiler (Ambios Technology Inc., XP-2). Optical transmission was measured in the 200–900 nm range by using an UV/V spectrometer (Lambda 900 UV/VIS/NIR SPECTROMETER). The surface morphologies of samples were observed by scanning electron microscope (SEM) (Hitachi, S-4800).

3. Results and discussion

3.1. The structures of AlSb films

The XRD patterns of two kinds of AlSb thin films are shown in Fig. 1. The XRD analysis revealed that the films are polycrystalline of zinc–blende structure with peaks at $2\theta = 25.03°$, 41.61°, 49.21° corresponding to C(111), C(220), and C(311) orientations, respectively. In both the two films the (111) peaks are the most intense peaks which imply that the crystals grow up preferentially along the ⟨111⟩ direction. When the film was deposited at 450 °C without an annealing, the (111) peak increases pronouncedly while (222) peak decreases slightly. Both the (200) and (222) peaks are very weak in the two films. No diffraction peak corresponding to metallic Al, Sb or other compounds was observed.

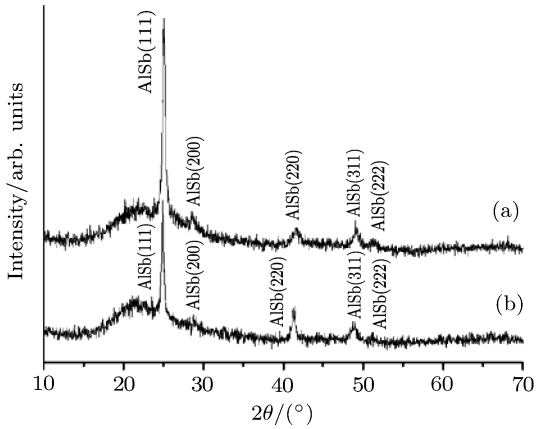


Fig. 1. The x-ray diffraction patterns of AlSb films deposited at different substrate temperature: (a) 450 °C without annealing, (b) 30 °C and then annealed in H_2 + Ar at 450 °C.

The lattice constant (α) was calculated from the (111) peaks of the XRD spectra with the following equation:[3]

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}, \tag{1}$$

$$2d \sin\theta = \lambda, \tag{2}$$

here d is the distance of the two adjacent (111) planes and $\lambda = 0.154$ nm. The lattice distortion $\Delta d/d_{\rm hkl}$ is defined in terms of $d_{\rm experimental}$[13]

$$\frac{\Delta d}{d_{\rm hkl}} = \frac{d_{\rm experimental} - d_{\rm hkl}}{d_{\rm hkl}}, \tag{3}$$

here $d_{\rm experimental}$ is the experimentally measured distance of planes and $d_{\rm hkl}$ is unstained lattice constant (0.61355 nm).[3] It was calculated that the lattice constant of sample (a) is 0.61562 nm with the distortion of 3.37% and that of sample (b) is 0.61692 nm and 5.49%, respectively. The grain size D was calculated by using the Debye–Scherrer formula:[3]

$$D = \frac{0.9\lambda}{(B\cos\theta_{\rm B})}, \tag{4}$$

here $\lambda = 0.154$ nm and B is the full width at half maximum (FWHM) of the peaks at the diffraction angle of $2\theta_{\rm B}$. The average grain size of (a) film is about 21 nm and that of the (b) film is about 12.4 nm. From the above analysis, it is seen that the lattice constant decreases, but the average grain size increases when the films were deposited at 450 °C without an annealing.

The SEM measurements are carried out to determine the surface morphology of AlSb films. From the SEM measurements in Fig. 2 it can be seen that both films are continuous, homogeneous with high compactness. The grain size of sample (a) is a little larger than sample (b) which is in agreement with the XRD results.

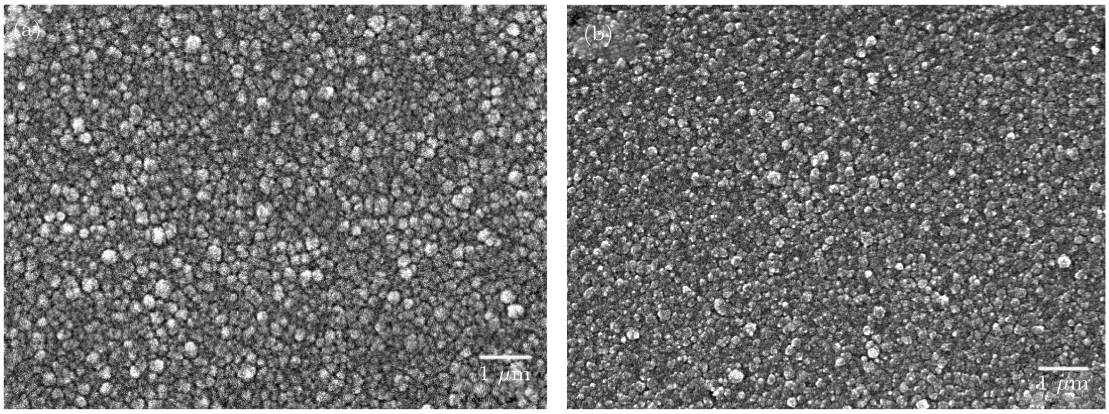


Fig. 2. The SEM analysis of AlSb films deposited at different substrate temperature: (a) 450 °C without annealing; (b) 30 °C and then annealed in H_2+Ar at 450 °C.

3.2. Electrical properties

The electrical property of AlSb film is an important aspect of the performance of AlSb solar cells. For the polycrystalline semiconductor films, the dark conductivity can be presented as[14]

$$\sigma_{\rm dark} = \sigma_0 \exp(-E_{\rm f}/kT) \exp(-E_{\rm b}/kT), \quad (5)$$

$$\sigma_{\rm dark} = \sigma_0 \exp(-E_{\rm a}/kT), \quad (6)$$

where $E_{\rm a}$ is called as conductivity activation energy and $E_{\rm a} = E_{\rm f} + E_{\rm b}$, $E_{\rm f}$ is Fermi energy, $E_{\rm b}$ is activation energy of carrier mobility and $\exp(-E_{\rm b}/kT)$ describes the temperature dependence of carrier mobility. Hence, $E_{\rm b}$ is just the average boundary barrier.

Figure 3 shows the $\ln(\sigma_{\rm dark}) \sim 1/T$ curves of AlSb polycrystalline thin films which were deposited at different substrate temperatures. The $\sigma_{\rm dark}$ and $E_{\rm a}$ have been calculated from Eq. (4) and the results are shown in Fig. 2. From the curves, it is seen that $\sigma_{\rm dark}$ decreases with the increase of temperature, this fact indicates semiconducting behaviour. For both the films, the experimental curves of $\ln(\sigma_{\rm dark}) \sim 1/T$ in the temperature decreasing process are straight-line and the values of $E_{\rm a}$ agree well with 0.32 eV deserved by co-evaporation.[2] Obviously, sample (a) which was deposited at substrate temperature of 450 °C shows less deviation from 0.32 eV in contrast to sample (b).

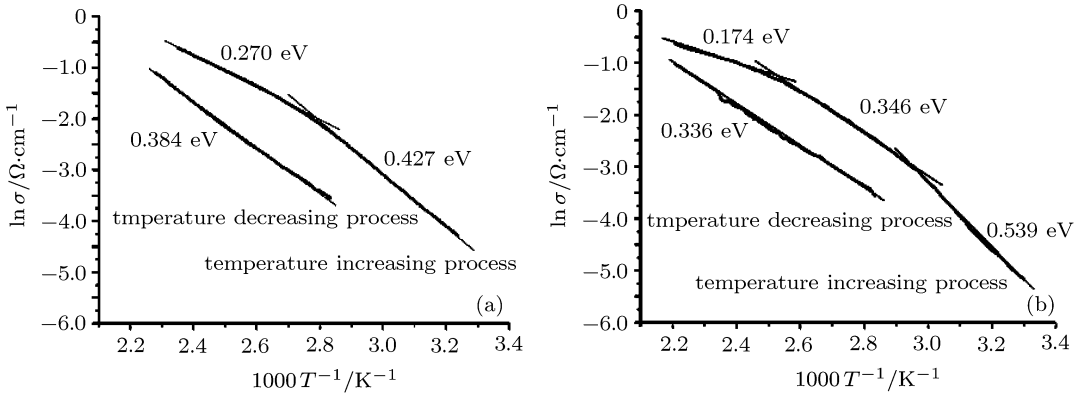


Fig. 3. $\ln(\sigma_{\rm dark}) \sim 1/T$ curves of AlSb polycrystalline thin films deposited at different substrate temperatures: (a) 450 °C without annealing; (b) 30 °C and then annealed in H_2+Ar at 450 °C.

3.3. Optical properties

According to the theory of optical interband transitions (direct or indirect) in solids, near the absorption edge, the absorption coefficient varies with the photon energy $h\nu$. Optical band gap of the film was calculated with the help of transmission spectra and reflectance spectra by using Tauc (1974) relation[15]

$$Ah\nu = A(h\nu - E_{\rm g})^n, \tag{7}$$

where α is the absorption coefficient, $E_{\rm g}$ the optical band gap, the constant A is 1/2 for direct band gap material and n is 2 for indirect band gap, the extrapolation of straight line to $(\alpha h\nu)^{1/2} = 0$ axis gives the value of energy of band gap. The value of the optical band gap $E_{\rm g}$ was taken as the intercept of $(\alpha h\nu)^{1/2}$ vs. $(h\nu)$ at $(\alpha h\nu)^{1/2} = 0$. The optical band gap derived for the film is 1.6 eV. The value of 1.6 eV is in a good agreement with the theoretical value of 1.62 eV[1] and 1.6 eV is higher than those obtained by co-evaporation or magnetron sputtering method, this fact indicates that the AlSb thin films prepared by co-sputtering with optimized deposition parameters have better optical properties.

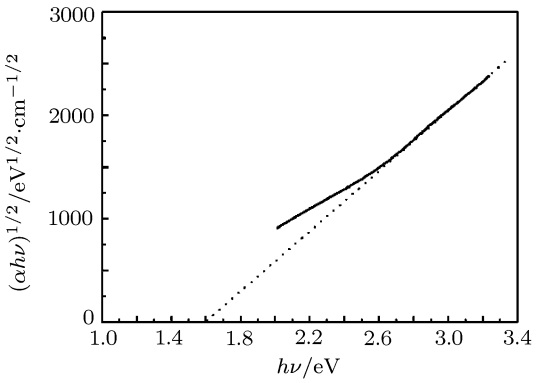


Fig. 4. Photon energy $(h\nu)$ vs. $(\alpha h\nu)^{1/2}$ for indirect band gap material of AlSb thin film deposited at 450 °C without annealing.

4. Conclusions

AlSb polycrystalline films have been prepared by magnetron co-sputtering method at different substrate temperatures with varying annealing parameters. The XRD analysis revealed that sample (a) prepared at a substrate temperature of 450 °C without an annealing exhibits an enhanced grain growth with an average grain size of 21 nm and the lattice constant is 0.61562 nm with the distortion of 3.37% in contrast to sample (b) of 0.61692 nm and 5.49%, respectively. The $\ln(\sigma_{\rm dark}) \sim 1/T$ curves show that the conductivity activation energy of sample (a) is about 0.38 eV with less deviation from 0.32 eV in contrast to sample (b). The transmittance and reflectance spectra show that AlSb thin film deposited at 450 °C without an annealing has an optical band gap of 1.6 eV. These results indicate that we have successfully prepared AlSb polycrystalline films without annealing.

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