Stable and low resistive zinc contacts for SnS based optoelectronic devices

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ABSTRACT

The contact behavior of tin mono sulfide (SnS) nanocrystalline thin films with zinc (Zn) and silver (Ag) contacts was studied. SnS films have been deposited on glass substrates by thermal evaporation technique at a growth temperature of 300 °C. The as-grown SnS films composed of vertically aligned nanocrystallites with a preferential orientation along the <010>-direction. SnS films exhibited excellent chemical stoichiometry and direct optical band gap of 1.96 eV. These films also exhibited excellent Ohmic characteristics and low electrical resistivity with Zn contacts. The observed electrical resistivity of SnS films with Zn contacts is 22 times lower than that of the resistivity with Ag contacts. The interfacing analysis reveals the formation of conductive Zn–S layer between SnS and Zn as interfacial layer.

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1. Introduction

Tin monosulfide (SnS) is a narrow band gap (1.35 eV) semiconductor material [1,2]. SnS has received great attention in the field of solar energy conversion due to its low toxicity, abundance in nature, and possible high light conversion efficiency (~28%) [3]. However, the achieved highest light conversion efficiency of SnS based solar cell devices, as of today, is far from its theoretical value (~2%) [4–7]. This is attributed to various factors including poor quality and high resistance of SnS, and its lattice mismatch with window layers like Si based solar cell devices [8]. The metal–semiconductor contact resistance also plays a great role on the performance of devices. For example, in the case of solar cell devices, it is essential to use non-rectifying metal contacts with low resistance since the back contact resistance mainly influences the total series resistance of the device and thereby reduces the efficiency. Therefore, low resistive Ohmic contacts are highly required for the realization of efficient SnS based devices.

Over the past few years there has been a growing interest in the metallization of SnS films and a few groups have also observed interesting results [9–12]. For example, the contact behavior of highly sulfur-rich SnS films grown on indium doped tin oxide (ITO) substrates by pulsed electrochemical deposition has been studied with different metal contacts including aluminum (Al), silver (Ag), gold (Au), and indium (In) [9]. With all these contacts excellent Ohmic electrical characteristics between the bias voltage of −1 and +1 V and a high current in the order of few mA have been observed. Further, a decrease in the contact resistivity with the increase of annealing temperature has also been observed. On the other hand, Devika et al. [10] have studied the metallization of thin SnS films grown on glass substrates with different non-alloyed metal films (M = Ag, Al, In and Sn). Here all the metal contacts were deposited with a thickness of 50 nm by thermal evaporation method at a substrate temperature of 50 °C. From all SnS/M structures, except SnS/Ag, they have noticed an excellent Ohmic contact behavior between −10 and +10 V. In the case of SnS/Ag contacts the Ohmic behavior has been observed only between −6 and +6 V. The electrical resistivity of SnS films with Ag, Al, In, and Sn contacts was found to be 26, 17, 5, and 9 Ω cm respectively. However, while annealing the SnS/M structures (300–500 °C), a drastic degradation in the overall electrical properties of SnS/In and SnS/Sn structures and good stability in SnS/Ag with a low resistivity (1.15 Ω cm) have been observed. These results clearly emphasized the necessity of compatible, low-resistive (10−2 Ω cm) and thermally stable Ohmic contacts (~300 °C) for SnS films. Thus, we made an attempt to find an appropriateness of zinc (Zn) metal contacts as Ohmic for SnS films and reported their current–voltage characteristics here.
2. Experimental procedure

SnS films were deposited on glass substrates by thermal evaporation technique at 300 °C with a thickness of 250 nm under the optimized conditions reported elsewhere [13]. After preliminary analysis with Bragg’s X-ray diffraction (XRD, model: Phillips X’Pert Pro with Cu Kα radiation with λ = 0.1541 nm), field emission scanning electron microscopy (FESEM, ZEISS ULTRA 55, Gemini, at voltage = 10 keV) and energy dispersion of X-ray spectroscopy (EDS, Oxford Instruments by applying 15 keV acceleration voltage under 10 mm working distance) attached to FESEM, micro Raman spectroscopy (LabRAM HR (HORIBA JOBINYUON)) and UV–vis spectrophotometer (Perkin Elmer, Lambda 35), two of the specimens were chosen and Zn metal contacts were thermally evaporated on one sample using mica sheet as mask at the temperature of 100 °C and silver (Ag) contacts were prepared on the other sample using silver paste. Here, the gap between two zinc and Ag contacts (d) was about 1 and 0.4 cm, respectively. The electrical properties of both the samples were measured at room temperature (RT) as well as different temperatures by using probe station attached with semiconductor analyzer (Agilent Device Analyzer B1500A).

3. Results and discussion

X-ray diffraction profile (XRD) (Fig. 1a) of SnS films exhibited a single diffraction peak at 2θ = 31.85° and the interplanar spacing (d-spacing) is found to be 0.281 nm. It indicates that SnS films have unique crystallites that are preferentially oriented along the <010> direction.

The cross sectional analysis reveals that SnS films have vertically aligned nanocrystals (Fig. 1b) with an average length and diameter of 250 and 100 nm, respectively. Composition analysis shows that the films have good chemical stoichiometry and the Sn/S atomic ratio is about ~1.04. The Raman spectrum of SnS films exhibited six distinguishable peaks (Fig. 2), which are assigned to various optical phonon modes of SnS. This indicates that SnS films clearly consist of pure single phase. The optical studies (Fig. 3) show that these films have a direct optical band gap (EgD) of 1.96 eV, which is slightly higher as compared to SnS films grown by other methods [13].

Current–voltage (I–V) characteristic plots of the films with Ag and Zn contacts measured at RT are shown in Fig. 4. The electrical resistivity of SnS films was evaluated from the inverse slope of linear curve and is found to be ~90 and 4 Ω cm with Ag and Zn contacts, respectively. Here, the electrical resistivity of SnS films with Zn contacts is nearly 22 times lower than the value obtained with Ag contacts and comparable with the In and Sn contacts. Apart from this, the observed electrical resistivity of SnS films with Zn contacts is quite low as compared to that of the films even deposited on ITO substrates by using the constant-current electrodeposition (~7 Ω cm) [14]. Similarly to the present results, Calixto-Rodriguez group also observed a high electrical resistivity (~10^4 Ω cm) for SnS films deposited by spray pyrolysis on glass substrates using Ag past as contacts [15].

The observed low resistivity of SnS films with Zn contacts is probably attributed to the work function of Zn and/or the barrier height between SnS and Zn. The energy band diagram of SnS/Zn and Ag is shown in Fig. 5. This reveals that the Fermi level of Zn metal pins at above the Fermi level of SnS (~0.57 eV) and its barrier height (φBn) is found to be 0.87 eV [10]. In the case of
Ag, the Fermi level pins slightly below the valence band of SnS (~0.32 eV) and the barrier height is found to be ~0.02 eV (here we considered SnS electron affinity ($\chi_{SnS}$) as 3.2 eV for bulk, and 2.5 eV for present nano films). Noticeably, as mentioned in Introduction [10], the observed low electrical resistivity of SnS films particularly with In contacts probably attributed to its low work function (~3.83 eV), and high resultant barrier height (~0.67 eV). From these results it can be highlighted that the conductivity of SnS films strongly depends not only on the work function of metal contacts but also on their resultant barrier height.

In order to understand the nature of surface morphology of Zn metal contacts and the chemical composition at SnS/Zn interface, the structures were examined with field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) and the obtained results are shown in Fig. 6. Fig. 6a shows that the surface of Zn contacts on SnS films consists of fine hexagonal micro-crystallites, which are tightly bonded together and formed a smooth surface. The spatial distribution of the atomic contents across the SnS/Zn interface, obtained by line-scan elemental mappings of Sn, S and Zn, is shown in Fig. 6b. The profiles of Sn and S (red and green) show sharp peaks, while the profile of Zn (blue) shows broad peak at the right side and sharp interface with SnS at the left. The thickness of SnS film and Zn contact are found to be ~240 nm and ~3 μm, respectively. This analysis clearly shows the well defined composition variation and a clear interfacing between SnS and Zn layers. From the careful observation of Fig. 6b, it can be seen that the Zn metal slightly diffused into SnS layer and its diffusion length is found to be ~20 nm. These results, therefore, reveal that while depositing Zn contacts on SnS films the Zn atoms diffused into SnS, and probably formed highly conductive ZnS compound as interfacial layer. This clearly supports the current flow between SnS and Zn.

The temperature dependent resistance of SnS films with Zn and Ag contacts was measured in the range of 20–200 °C and is shown in Fig. 7a. The lowest electrical resistivity of SnS films with Zn and Ag contacts at 200 °C are found to be 0.49 and 8.2 Ω cm. The activation energy ($\Delta E$) of SnS films with both the contacts were evaluated by fitting the experimental data to the Arrhenius' equation (Fig. 7b) and is found to be the same value of about ~0.24 eV. For more details about the variation of electrical resistivity and activation energy of SnS films with different metal contacts observed in the present as well as earlier studies see the data given in Table 1. From these results it can be concluded that the best device performance can be obtained by choosing Zn as Ohmic contacts for the SnS based photovoltaic devices. However, before the adoption of Zn contacts for the development of SnS based optoelectronic devices there are various issues like influence
of Zn contact thickness, its stability with annealing temperature, and selection of protective layer for this highly reactive contacts has to be investigated, which are in progress.

4. Conclusions

Stoichiometric SnS films were deposited on glass substrate by thermal evaporation method and then, Zn and Ag contacts were deposited. The electrical characteristics of SnS films with both contacts were studied at RT as well as at different temperatures. As compared to the existing data, the electrical resistivity of SnS films with Zn contacts is low (~4 Ω cm). While increasing temperature the resistance of SnS films with both the contacts decreased and showed the same activation energy of 0.24 eV. From these results it is concluded that by adopting Zn contacts as Ohmic contacts one can realize better performance from SnS based photovoltaic devices.

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