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$CuInSe_2$ formation through Cu_2Se–In_3Se_2 multilayer structures prepared by thermal evaporation technique

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The current study investigates the Cu_2Se/In_3Se_2 multilayer structure deposited by thermal evaporation technique for CIS solar cells with different number of layers. The X-ray diffraction pattern reveals that the layer thickness improves the crystallinity and the formation of CIS for the 30 layer films through photoluminescence (PL) emission. The optical band gap values are found to be 2.87 eV and 2.79 eV for 5 and 10 period films respectively. The splitted band gap ranging 1.30 and 2.25 eV for 15 periods and decrease in the band gap values are due to large grains. This splitting is due to quantum size effect and CIS composite formation. The vibration frequency at 174.54 cm^{-1} is evident for formation of $CuInSe_2$ Chalcopyrite phase.

1. Introduction

In recent years, multilayer thin film semiconductor structures have a great attraction to develop emerging devices especially in the optoelectronics. It can provide information to study quantum size effects and confinement effects. Artificially, multilayered thin film structure was composed of the two different semiconductors stacked with the alternating layers in the nanometer range of thickness [1–2]. These kind of multilayer structures have unique and attractive properties due to their reduced dimensions. Their optical and electronic properties strongly depend on the thickness and physical parameters. It is possible to achieve the novel and unique properties through multilayer structure. Especially, a 2-D nanostructured semiconductor thin film has great attention due to their structure dependent optical and electrical properties [3,4]. This can be useful to fabricate the next generation electronic devices predominantly solar cells. Recently, multilayer structures have been investigated with the different combination of materials such as CdSe/ZnSe [5], ZnSe/PbSe [6,7], CdSe/Se [8], Ge/Si [3] and TiO_2–Ge [9]. The new novel materials and nanostructure are needed to develop potential application such as solar cell and optoelectronic devices. CIS formation through stacking multilayers of CuSe and InSe is presented in this paper. In this present work, CIS has been formed by depositing Cu_2Se/In_3Se_2 multilayers. This multilayer approach has the possibility of precise control of the sub monolayer thickness during the deposition process. The structural, optical and morphology were investigated for different periods of layers.

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2. Experimental details

Cu_2Se/In_3Se_2 multilayer structure has been subsequently deposited by thermal evaporation technique on glass substrates at room temperature. The high purity base materials were purchased (In_3Se_2) in the form of ingot (sigma Aldrich-99.99%) and Cu_2Se as pellets (Alfa Acer- 99.99%). The source materials were kept in two separate molybdenum boats (200 amps) and the distance between boats to substrate was maintained as 28 cm. Initially In_3Se_2 was deposited on the substrate with a thickness of 50 nm to act as a buffer layer. The thickness of Cu_2Se (10 nm) and In_2Se_3 (50 nm) layers was fixed. Then a Cu_2Se layer was deposited on top of the buffer layer followed by In_3Se_2 layer. These layers were alternatively deposited and the cycle was repeated to obtain several periods of layers 5, 10 and 15 without breaking the vacuum. The layer thicknesses were monitored and controlled by an in-situ quartz crystal thickness monitor. A constant rate of evaporation ranging between 1 and 3 Å/s was maintained throughout the experiments. Finally, the multilayer sample was carried for structural, optical and morphological studies. The structural properties were analyzed by X-Ray diffraction using Cu $K\alpha$ radiation (Shimadzu XRD-6000 X-ray Diffractometer) diffraction ranging from 10°–90°. The surface morphology was examined by scanning electron microscopy (Jeol) and composition of elements was analyzed by Energy Dispersive X-ray analysis. The optical properties was studied by UV–VIS–NIR spectrophotometer (Jasco-570 UV/VIS/NI Spectrophotometer) in the range of 200–2500 nm. Photoluminescence (PL) emission were studied by Spectroflurometer (JASCO FP-8200) recorded in the range between 200 and 900 nm. Raman Scattering was studied using LabRAM HR 800 micro Raman Spectrometer with 514.12 nm laser source (see Fig. 1).

3. Result and discussion

3.1. X-ray diffraction analysis

Fig. 2(inset) shows the reference Cu_2Se and In_3Se_2 XRD patterns. The sharp intense peaks in Cu_2Se oriented towards (221) perfectly match with JCPDS – 530523 and which reveals the film is cubic crystalline nature. In Fig. 2(inset) shows the peaks correspond to (110), (300) exactly matches with JCPDS – 678906 and which indicates presence of In_3Se_2 phase with hexagonal crystal structure.

Fig. 2 shows the X-ray diffraction pattern of as deposited Cu_2Se - In_3Se_2 multilayers films. In Fig. 2(a) and (b) a broad hump indicates amorphous nature. Fig. 2(c) shows that peak (1 1 2) identified at ($2\theta = 26.62$–26.51). Further confirmation is done through laser Raman studies in the later part of this paper. The peak corresponds to tetragonal chalcopyrite of $CuInSe_2$ (JCPDS – 657027). The peak (1 1 2) was shifted slightly towards the lower angle. This may be due to the contraction of lattice constant induced by increasing films thickness [10]. In Fig. 2(c) additional secondary peaks corresponds to (2 0 4) at 45.15° which is the characteristic peak of InSe with hexagonal crystal structure. The lattice parameter of multilayers are gradually decreases as no of layers increases (15 period films) which indicates the strain relaxation. However, the position of these peaks is slightly shifted to lower angles with increasing number layers. Its noteworthy to state that the intensity of the (1 1 2) peak increase with increasing number of periods of layers, which depicts evaluation of CIS phase. From the shift in CIS orientation towards lower angle indicates decreasing tensile strain due to increase in number of periods of layer [6]. This attributes to the strain induced crystallization mechanism [11,12].

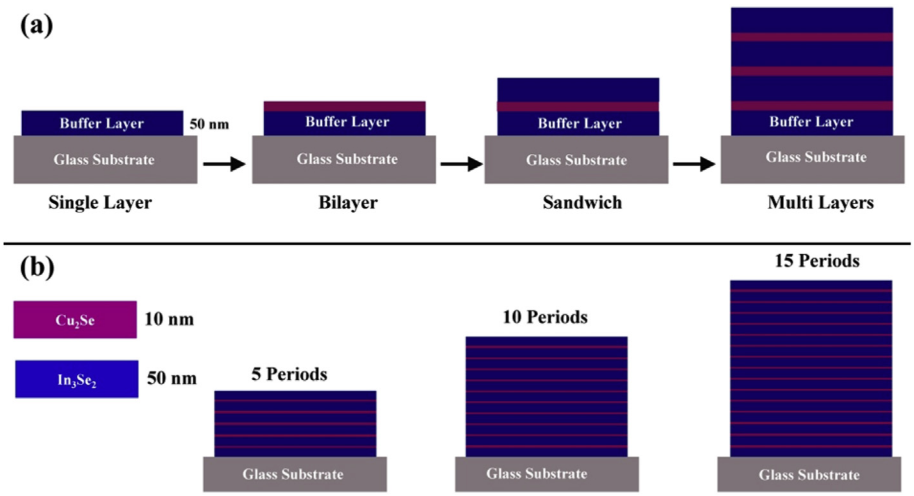

Fig. 1. Schematic of Cu_2Se–In_3Se_2 multilayer films (a) stack of alternate layers of Cu_2Se–In_3Se_2 (b).