Nickel diffusion in polycrystalline CuInSe$_2$ thin films with a <112> fiber texture

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A B S T R A C T

Nickel diffusion in CuInSe$_2$ thin films was studied in the temperature range 430–520 °C. Thin films of copper indium diselenide (CuInSe$_2$) were prepared by selenization of CuInSe$_2$–Cu–In multilayered structure on glass substrate. A thin film of Nickel was deposited and annealed at different temperatures. Surface morphologies of the Ni diffused and undiffused CuInSe2 films were investigated using scanning electron microscope. The alteration of Nickel concentration in the CuInSe$_2$ thin film was measured by Energy Dispersive X-Ray Fluorescence (EDXRF) technique. These measurements were fitted to a complementary error function solution and the diffusion coefficients at four different temperatures were evaluated. The diffusion coefficients of Ni in CuInSe$_2$ films were estimated from concentration profiles at temperatures 430–520 °C as $D = 1.86 \times 10^{-7} (\text{cm}^2\ s^{-1}) \exp[-0.68(eV)/kT]$.

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1. Introduction

Polycrystalline CuInSe$_2$ semiconductor has become a leading material for large scale thin film solar cell applications because it has a direct band gap, high absorption coefficient and good thermal stability. CuInSe$_2$ has received considerable attention as one of the most promising materials for second-generation solar cells. Currently, efficiencies of greater than 19% have been achieved [1]. However, the low yield and adhesion of CuInSe$_2$ thin film with the back contacting layers are major problems which deteriorate the production quality of CuInSe$_2$ thin films. The most common materials used for the back contact layers to CuInSe$_2$ are Au, Ti, Mo, Al, Ni, Ag, Pt and Cu elements. Studies show that Au, Ti, Mo, Pt and Ni all form fairly reproducible low resistance contacts to CuInSe$_2$. However, Au, Ti and Pt show significant diffusion into CuInSe$_2$ during annealing at elevated temperatures and, thus, only Ni and Mo have emerged as valid candidates for use as ohmic contacts in these cells [2–4].

The mechanism of diffusion in thin films is generally different from that in the bulk sample. Diffusion in thin films can be through the grain or along the grain boundaries depending upon the microstructure of thin films. When diffusion is generally via the grains in films with large grains, the analysis gives the lattice diffusion coefficients. As the grain size decreases, atomic transport also occurs

along the grain boundaries and the analysis yields grain boundary diffusion parameters [5].

The native point defects (such as Cu, In and Se vacancies), the linear and the surface defects (dislocations, grain boundaries etc.) are the characteristics of polycrystalline CuInSe$_2$ thin films. These defects present channels for the fast migration of impurity atoms. Processes of nickel diffusion penetration into thin CuInSe$_2$ film caused by thermal annealing during CuInSe$_2$ based solar cells preparation or by photo-treatments under the sunlight exploitation can cause degradation of characteristics of the devices [6–10].

In this study, the diffusion of nickel in CuInSe$_2$ thin films was investigated in the temperature range 430–520 °C. The activation energy was calculated via Arrhenius plot of diffusion coefficients.

2. Experimental procedure

The starting materials of CuInSe$_2$ were synthesized from a stoichiometric mixture of its constituent elements. Copper, indium and selenium of 5N purity were put in a sealed quartz ampoule evacuated to a pressure of 0.13 Pa. The mixture was heated in a vertical furnace initially to a temperature of 200 °C and kept there for 8 h to ensure the good homogeneity and to avoid the risk of explosion due to the exothermic reaction of indium and selenium. Then, the temperature was slowly increased to 1200 °C and was maintained there for 15 h. Finally, the ampoule was quenched to room temperature. The ingot obtained was pulverized and made into small pellets for evaporation.

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Thin film samples were prepared in two steps. In the first, $CuInSe_2$ thin films were prepared by vacuum evaporation on glass substrates at 450 °C. In the second, $CuInSe_2$ thin films were covered with Cu and In layers by sequential evaporation at room temperature. Then the obtained multilayer structures were subjected to selenization procedure; the temperature of the structure was raised to 150 °C (below the melting point of In) and kept at this temperature for 1 h in order to make interdiffused Cu and In layers. Then the temperature was raised up to the selenization temperature (520 °C). During the selenization, the temperature of the Se source was kept at 200 °C [6,11].

To investigate crystallographic properties of the films, coupled $\theta–2\theta$ X-ray diffraction (XRD) scans were performed in the range of $2\theta = 3–70°$ by using the CuK_α line of the X-ray source.

Nickel diffusion in $CuInSe_2$ thin films was carried out for 10 min using *a* vacuum evaporated layer of Ni on the open surface of the thin films. The diffusion annealing of the films with the deposited layer of nickel was performed under a dry argon atmosphere in the temperature range 430–520 °C. After annealing, the remainder of the Ni layer on the upper $CuInSe_2$ surface was removed by using HNO_3: H_2SO_4: H_2O (5: 5: 90) solution and the lateral sides of $CuInSe_2$ films were cleaned by grinding.

To determine the alteration of Nickel concentration in the $CuInSe_2$ thin films, thin layers were removed successively from the sample by using a HF: H_2O (1:2) solution and then after each removal process the Nickel concentration was measured from its K_α (7.48 keV) X-ray line by using energy dispersive X-ray fluorescence (EDXRF) technique. A detailed description of the system can be found in the literature [12]. The amount of Ni in the first removed layer was obtained from the integrated intensity of the NiK_α line from the remaining film when this intensity was subtracted from the NiK_α integrated intensity obtained from the unetched film. The similar procedure was applied for other layers.

Scanning electron microscopy (SEM) was performed for determining the microstructure of the films, using a JEOL JEM-5510 operating at an accelerating voltage of 15 kV. The thickness of each thin film after each removal process was calculated as described in the Ref [13]. The thin film samples were irradiated by 59.5 keV photons emitted by an annular 50 mCi ^{241}Am radioactive source to obtain NiK_α X-rays (7.48 keV) emitted from the samples. A Si(Li) detector (full width at half maximum 147 eV at 5.9 keV, active area 13 mm^2, thickness 3 mm and Be window thickness 30 μm) was used to count the emitted K_α X-rays.

3. Results and discussion

<112>, <220> and <116> diffraction lines were used to determine the lattice parameters in $CuInSe_2$ films. One can conclude from Fig. 1 that the polycrystalline films have strong <112> fiber axes. X-ray
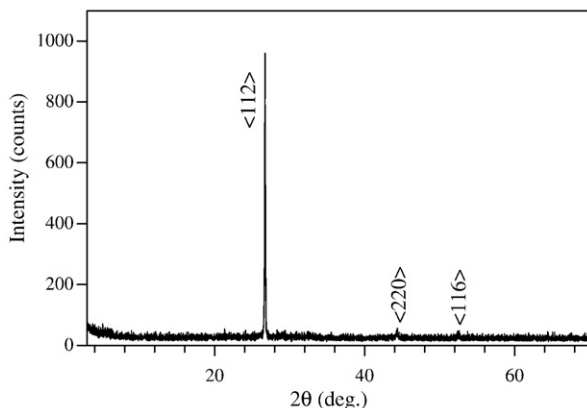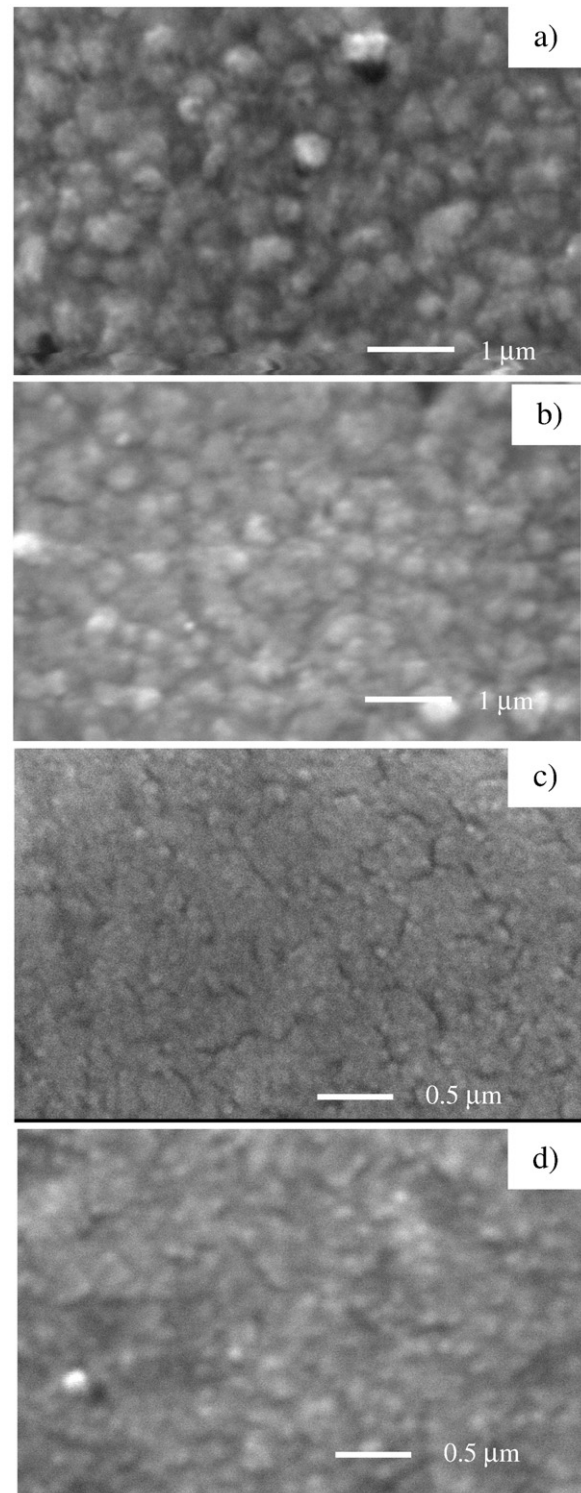

Fig. 2. SEM photographs of (a) $CuInSe_2$ (b) etched $CuInSe_2$ (c) Ni diffused $CuInSe_2$ (d) Ni diffused and etched $CuInSe_2$ thin films.

diffraction measurement showed that the polycrystalline $CuInSe_2$ thin films have chalcopyrite structure with lattice parameters $a = 5.57$ Å and $c = 11.55$ Å, and the direction of growth coincides with the <112> axis of the films (Fig. 1). These parameters show a good agreement with the literature.

SEM photographs of the films were given in Fig. 2(a) $CuInSe_2$ (b) etched $CuInSe_2$ (c) Ni diffused $CuInSe_2$ (d) Ni diffused and etched $CuInSe_2$ thin films. As seen from the pictures, the grain size was decreased with annealing (Ni doped).

Fig. 1. X-ray diffraction pattern of the $CuInSe_2$ thin film.