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Surface Modification and Doping Effects of Sb on the Growth of $CuInSe_2$ Films by Molecular Beam Deposition

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The growth of $CuInSe_2$ film in the presence of Sb-beam flux has a dramatic improvement in surface morphology and grain structure. It is attributed to the surfactant modified growth caused by the Sb atoms. A p-type $CuInSe_2$ film with a resistivity as low as 0.05 ohm-cm is obtained, which is comparable with the resistivity of a Cu-rich film grown without Sb.

1. INTRODUCTION

$CuInSe_2$ is the only I-III-VI_2 compound under intensive study because of its high potential in solar-cell applications [1-3]. High-efficiency $CuInSe_2$ solar cells had been realized by the use of two-layer $CuInSe_2$ structure, that is, a low-resistivity Cu-rich layer was first deposited on the Mo-coated glass substrate and then followed by a high-resistivity In-rich layer [2]. Surface morphology and grain structure of the top layer duplicated from the bottom layer which had a large-grain structure but rough surface [4]. This caused the problem for the deposition of n-type CdZnS film which was normally used to form a junction with p-type $CuInSe_2$. We attempt to solve this problem by the use of an impurity which may modify the surface morphology, preserve the large-grain structure, and serve as a p-type dopant. Antimony is such an element meet all these requirements. In this paper, the structures and properties of Sb-doped films are studied in some details. The effects of Sb on the surface processes during film growth are also discussed.

2. EXPERIMENTAL PROCEDURES

Thin films of $CuInSe_2$ were grown by molecular beam deposition(MBD). The background pressure of the MBD system was 4×10^{-9} torr after bakeout. The temperature of Cu source and Se source was kept at 1050°C and 210°C, respectively. The temperature of In source was varied from 720°C to 750°C in order to control the Cu/In ratio of the films. The temperature of Sb source was varied from 300°C to 550°C to find the optimum conditions for the improvements in grain structures. The substrate was heated by quartz lamps and the temperature was measured by a thermocouple attached near to the substrate. The temperatures of elemental sources and substrate were controlled by Eurotherm 818S controllers and the temperature variations were within 1°C. All films were grown on sodalime glass substrates and Mo-coated glass substrates.

X-ray diffractometer was used to identify the phases in the films and to determine the film textures. To perform microanalysis of the films, a JOEL 35C SEM equipped with EDX system was used. For trace element detection and elemental depth profiling, secondary ion mass spectroscopy (SIMS) was utilized for the analysis. Film resistivity was measured by four-point probe.

3. RESULTS AND DISCUSSIONS

3.1 Growth and Characterization of the Films

Near-stoichiometric $CuInSe_2$ films were grown under Se overpressure and the fluxes of Cu and In were independently controlled to obtain the films with desired Cu/In ratios. The surface morphology of the films depends on the film compositions as mentioned earlier. If the films grown in the presence of Sb-beam using the same conditions for growing Cu-rich film, the surface improved in smoothness as the Sb-beam flux increases. A mirror-like surface was obtained when the Sb flux above 5.0 x 10^{14} atoms/cm^2-sec was used for the growth.

Fig. 1a and 1b show the surface morphologies of the typical Cu-rich film and a film grown with the introduction of Sb-beam flux, respectively. As can be seen, the improvrment in the smoothness of the as-grown surface is significant. It is also observed that the grain structure of the film grown under the exposure of Sb-beam is compact and substantially reduce the porosity of the film. Such a change in surface features of the films is attributed to the change in growth modes from island growth to layer-by-layer growth. Further discussion will be given in the next section.

Since the Sb flux as high as 5.0 x 10^{14} atoms/cm^2-sec is used to obtain a Cu-rich film with mirror-like surface, the incorporation of Sb into the crystal lattice of the film has to be studied to see how it affects the film properties. X-ray diffraction data as well as EDX analysis did not detect any second phases or trace of Sb element in all films. It can only be detected by SIMS and the ion counts of Sb are high near the surface but decrease dramatically away from the surface, see Fig. 2. The results indicate that the incorporation probability of Sb is minimal and surface segregation is evident.

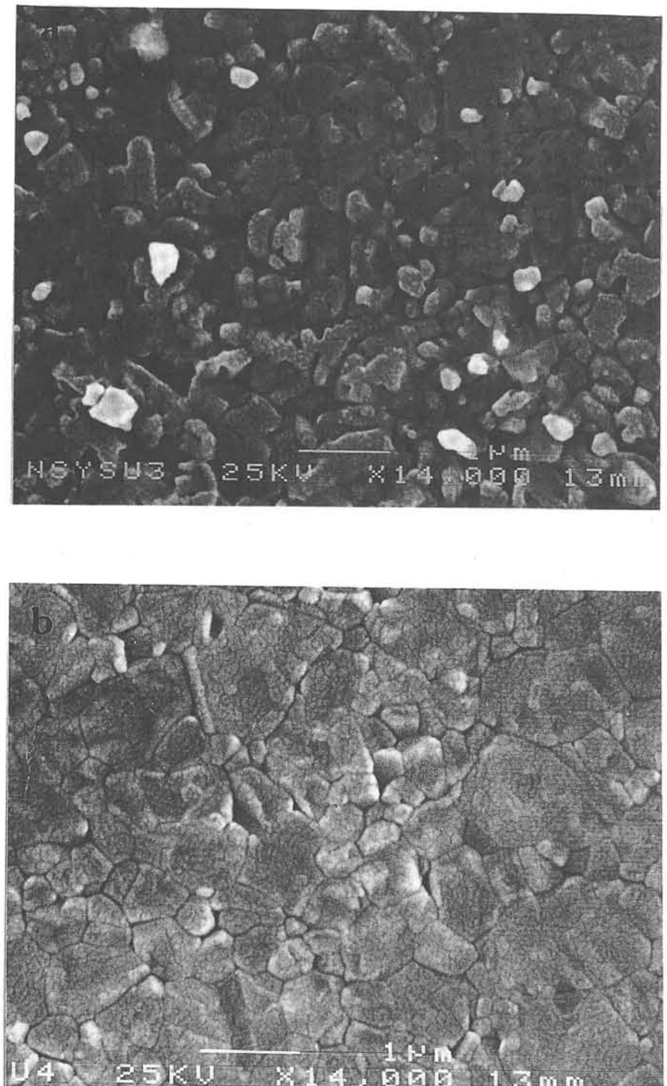

Fig. 1 SEM micrographs show the grain structures of the thin films (a) grown without Sb flux and (b) grown with Sb flux.

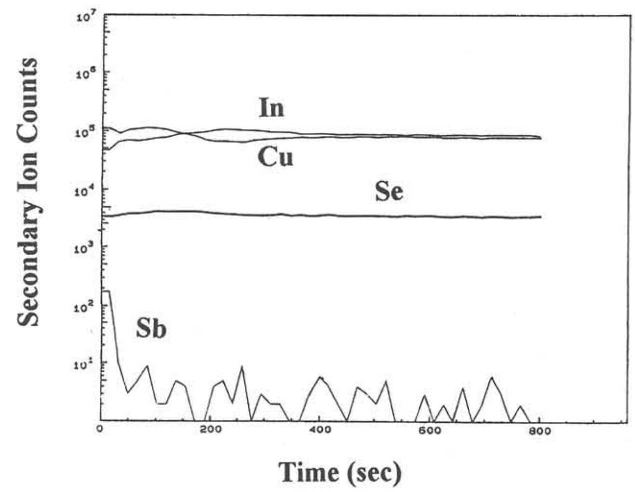

Fig. 2 Typical SIMS profiles show the elemental distributions in the film grown in the presence of Sb flux.

Resistivities of the $CuInSe_2$ films are closely related to chemical compositions [5,6]. Fig. 3 shows the resistivities measured from thin films grown with and without Sb versus their compositions. Cu-rich films were characterized to be p-type and low resistivities. When the composition is close to the stoichiometric value the resistivity increased dramatically. For films grown with Sb, the doping effect caused by Sb atoms (a p-type dopant to $CuInSe_2$) is distinct as the film is slightly Cu-rich. However, the effect of Sb doping may be overwhelming if the film becomes more Cu-rich. Even so, a p-type film with resistivity as low as 0.05 ohm-cm and mirror-like appearence can be obtained instead of a film with similar electric properties but rough on surface.

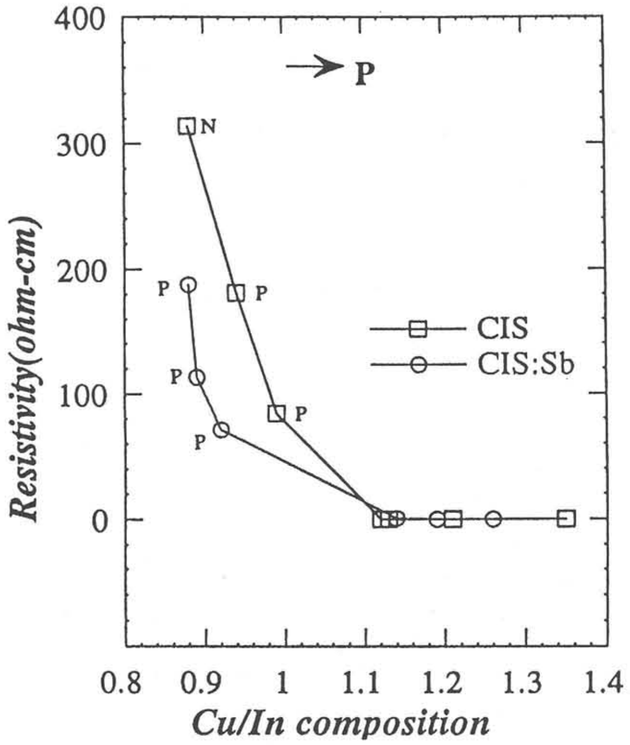

Fig. 3 Resistivities and conductivity-type of the films with various Cu/In ratios.

3.2 Modification of Surface Processes

The influence of Sb on the surface processes during film growth is evident. Based on the experimental results described above, we conclude that Sb acts as surfactant on the growth of $CuInSe_2$ film. The surfactant-controlled MBE growth had been reported in the Ge/Si system [7]. It reduces the surface free energy and "float" on the surface after growth. Thus, it promote a layer-by-layer growth mode and results in a smooth surface and densified grain structure. The facts that high Sb flux used but very low Sb concentration detected in the films and a decreased concentration gradient of Sb found in the film suggests high degree of surface segregation and very low sticking probability on surface.

To the best of author's knowledge, it is the first time to demonstrate the surfactant modified growth in a compound material. In our case, the films were mainly polycrystalline. Segregation of Sb not only occurs on the free surface but also along the grain boundaries. Thus, the film should be grown in a constant flux of Sb beam.

4. CONCLUSIONS

We have demonstrated that the growth of $CuInSe_2$ film in the presence of Sb-beam has a dramatic improvement in surface morphology and grain structure. It is attributed to the surfactant modified growth caused by the Sb atoms. A p-type $CuInSe_2$ film with a resistivity about 0.05 ohm-cm was obtained, which is comparable with the resistivity of a Cu-rich film grown without Sb. We believe that all the new features of the Sb-doped $CuInSe_2$ films will greatly improve the electric properties and result in an increase in energy conversion efficiecy of a solar-cell.

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