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doi:10.1017/S1431927615011472 Paper No. 1068
Microsc. Microanal. 21 (Suppl 3), 2015

Inter-Diffusion Characterization of SnO_x/CuO_x Grown on Cu Foil

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Hetero thin films junctions with multi band gaps have potential to improve the efficiency of solar energy absorption and photoelectrolysis [1, 2]. Considerable efforts have been made to fabricate stable thin film heterojunctions with different dopants. Elemental inter-diffusion on the hetero-junctions caused by thermal treatment is generally considered as undesirable for interface stabilities. However, elemental inter-diffusion may lead to a formation of gradient-alloyed thin films with band gap modification. This may result in various band gaps with wide range. Single layer CuO and SnO_2 thin films have received intensive attention because of their potential in cost-effective solar cell technology. CuO and Cu_2O, p-type semiconductors with band gaps of ~1.5 eV and ~2.0 eV respectively, have been materials of interest due to relatively high optical absorption and low cost [3]. SnO_2, an n-type semiconductor with a band gap of ~3.7 eV, is of interest because of its high optical transparency and low electrical resistance [4]. However, increased power conversion efficiency depends on the interfacial engineering of the junction, which requires a detailed understanding of Cu and Sn interfacial diffusion behavior.

In this research, CuO thin film was deposited onto a Cu foil via RF sputtering in a KJ Lesker thin film deposition system. SnO_2 film was deposited above the CuO film. The as-synthesized films were annealed in a furnace at 300˚C for one hour then in-furnace cooled overnight. Cross-section TEM specimens were prepared from the thin films with and without annealing via a dual beam FIB microscope. Imaging and composition analysis were performed at 200 kV on a FEI TECNAI F20 TEM with an Oxford SDD EDS detector and a Gatan Imaging Filter. XPS depth profile was carried out on a PHI VersaProbe II at a vacuum of ~1.2E-6 Pa, scanning 200 μm 15 kV 50 Watts X-ray beam, pass energy 23.5eV.

Before annealing, two apparent layers can be seen in Figure 1 a): about 250nm-thick CuO_x and 1250nm-thick SnO_x above the poly Cu foil. After annealing, three layers formed above the poly Cu foil. Beyond 290nm CuO_x and 223~375nm SnO_x layers, there is a 765~950nm inter-diffusion layer $Cu_xSn_yO_{1-x-y}$. Interestingly, this inter-diffusion layer is Sn-rich, as shown in Figure 1 b). An increase of about 50nm in CuO_x film is attributed to oxidation of Cu substrate during annealing. However, the thickness of SnO_x layer reduced from ~1250nm to ~223-375nm after annealing. It suggests that the inter-diffusion layer resulted from the diffusion of Cu into to SnO_x layer. It is interesting to note that little Sn diffused into the CuO_x layer. It indicates that Cu transportation in SnOx is much faster than that of Sn in CuO_x. Further quantitative EDS line scanning profiles shown in Figure 1c shows that the alloyed layer is Sn-rich oxide film with Cu alloyed. XPS depth profiles (Fig. 2a. and 2b.) were taken with pre-sputtered, annealed and non-annealed samples. The non-annealed sample had distinct regions showing little diffusion. The annealed sample had a more gradual onset of Cu signal in the Sn layer consistent with Cu diffusion into the Sn layer. In both cases, the Sn signal ceased promptly after the interface indicating little Sn diffusion into the CuO_x layer. The depth profile on the annealed sample was continued until the O signal was no longer present. This is consistent with the EDS analysis. Highly Cu alloyed SnO_x-based alloy film is formed between SnO_x and CuO_x layer. In the both annealed and non-annealed samples, XPS depth profiles revealed peaks from the CuO_x layer that are more consistent with Cu_2O rather than the CuO. This may be attributed to deposition in an oxygen-deficient environment under vacuum.

In conclusion, we found that after annealing a heterojunction of thin films of CuO and SnO_2 at 300˚C, Cu tends to diffuse into the SnO_x layer to form alloyed SnO_x but minimal Sn diffused into the CuO_x layer. SnO_x-based alloy thin film with Cu addition can be fabricated via simple thermal treatment. Future work would include variation of experimental parameters to tune the diffusion process and study its effects on the band structure of the heterojunctions. Continued efforts are being made to optimize power conversion efficiency in solar cell devices fabricated from CuO_x and SnO_x.

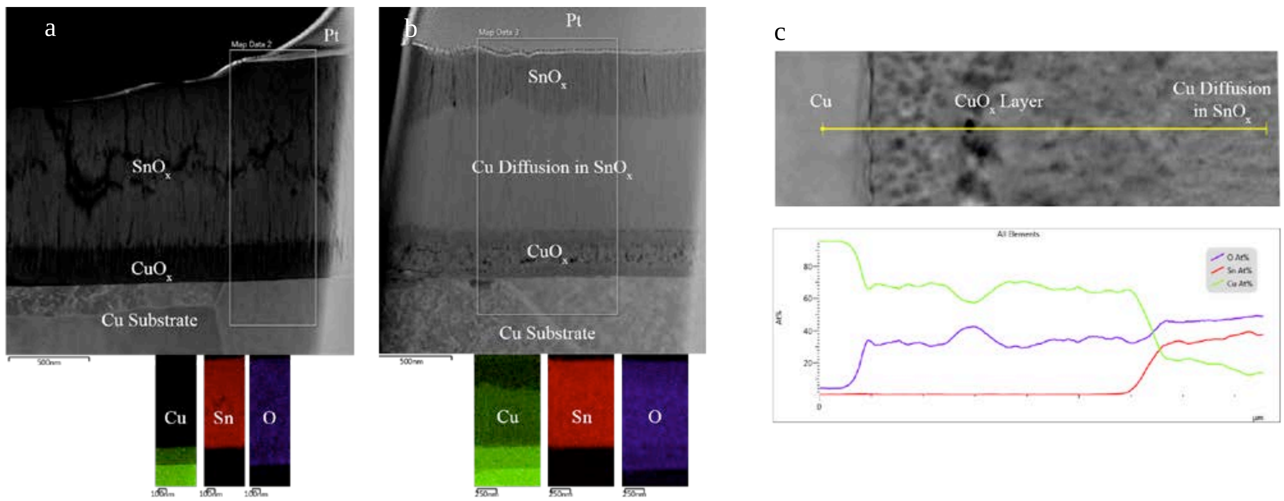

Figure 1. STEM HAADF micrographs and elemental maps by EDS of the a) non-annealed and b) annealed and an EDS line scan profile c) of annealed SnO_x/CuO_x. The annealed shows significant Cu diffusion into the SnO_x layer.

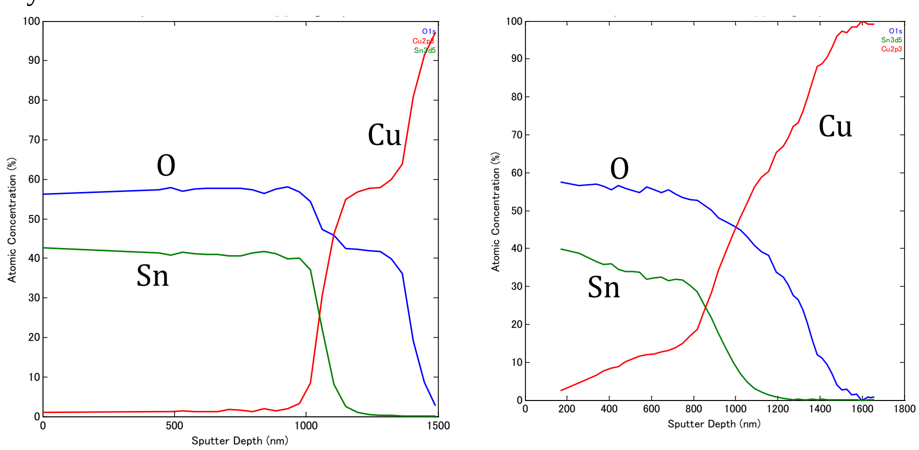

Figure 2. XPS depth profiles of the a) non-annealed and b) annealed SnO_x/CuO_x.

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