Preparation of Transparent Conducting Copper Aluminum Oxide Films

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Introduction:

Most optically transparent materials are electrical insulators. Transparent conducting oxides (TCOs) are exceptions and are used in optoelectronics such as photovoltaics and flat panel displays which need transparent electrodes. Currently, all mass produced TCOs are n-type, such as Sn-doped In_2O_3 and Al-doped ZnO. However, p-type TCOs are also necessary for electronic devices that require the entire p-n junction to be transparent, which would allow for devices that both generate electricity and transmit visible light (e.g. functional windows). P-type TCOs have been under study in recent years after the discovery of p-type conducting $CuAlO_2$ thin films by Kawazoe et al. with light transmittance of up to 70% [1].

However, most known ways of producing $CuAlO_2$ involve high temperature sintering of binary oxides for extended periods of time. In this project, $CuAlO_2$ synthesis was attempted using a DC-sputtering process employing elemental copper and aluminum targets. In this study, films were attempted by depositing Cu/Al bilayer films as well as co-sputtered films formed in the presence of oxygen. Only the co-sputtering process shows promise as a method of $CuAlO_2$ preparation, as the bilayer structure proved an ineffective route for production of such films.

Experimental Procedure:

Films were deposited using direct current (DC)-sputtering physical vapor deposition with a Kurt J. Lesker PVD 75 system, creating both bilayer and co-sputtered structures. To deposit the bilayer structure, a 50 nm layer of silicon dioxide (SiO_2) was grown on 2-inch silicon wafers to act as a diffusion barrier between the metallic film and substrate. Aluminum (Al) was deposited for 250 seconds at 300W for a 39 nm layer. Copper (Cu) was deposited for 43 seconds at 300W to form a 26 nm layer. These thicknesses were chosen to have a one-to-one stoichiometric equivalence of Cu and Al atoms in the bilayer structure. Samples were then annealed in an oxidation furnace for four to 12 hours at temperatures ranging from 400°C-900°C.

Reactive co-sputtering was employed to produce a single layer structure on glass substrate. Cu and Al were deposited simultaneously for 1000 seconds with Cu at 30W and Al at 60W. Deposition was performed in an argon/oxygen (Ar/O) atmosphere with oxygen content ranging from 2-10%. During the deposition process, the glass was heated to temperatures ranging from 100°C-300°C. Bilayer samples were characterized using x-ray diffraction crystallography (XRD) to determine composition. Co-sputtered samples were characterized using energy dispersive x-ray spectroscopy (EDX) to determine atomic composition, as well as UV-Vis spectrophotometry to characterize optical properties of the films at wavelengths between 300 nm and 1100 nm.

Results:

Films produced in the bilayer structure were shown by XRD to be composed primarily of Cu and Al oxides. $CuAlO_2$ reached a maximum purity of approximately 10% at 900°C annealed for 8h. Lower temperatures formed the binary oxides and CuAl alloy. Shorter annealing times also formed a large amount of unoxidized metal (Figure 1). At longer annealing durations, the SiO_2 barrier failed and metal diffused into the wafer forming silicides. Reactive co-sputtered films could not be characterized by XRD (Figure 2); this is an indicator that the films formed through this process were amorphous in nature [3].

UV-Vis showed the transparency of the co-sputtered films to decrease on average with increasing substrate temperature (Figure 3), and increase with the oxygen content present during deposition. Films formed at 100°C showed the highest level of transmittance, while those formed at 300°C and 2% O_2 showed the lowest. The higher oxygen content likely allowed for increased oxidation of the metals in the film to form the transparent $CuAlO_2$ phase. All films except those formed at 300°C and 10% O_2 displayed a peak at about 550 nm, caused by the Cu content in the films.

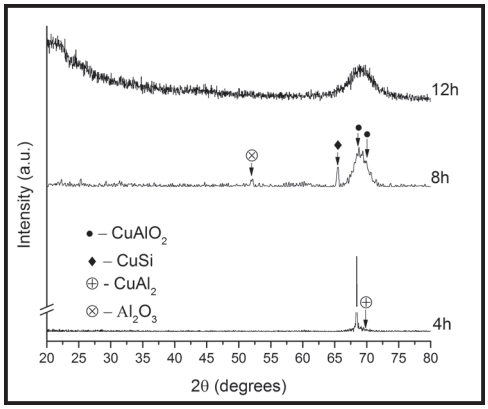

Figure 1: XRD of bilayer films at 900°C.

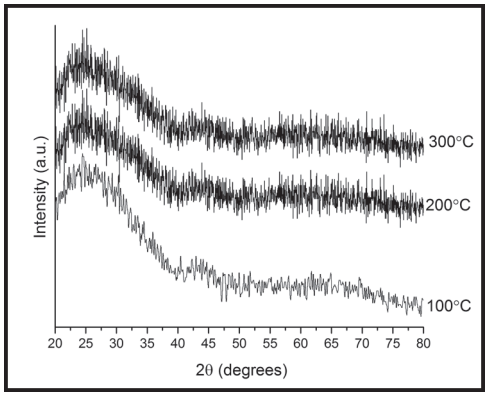

Figure 2: XRD of co-sputtered films in 5% O_2.

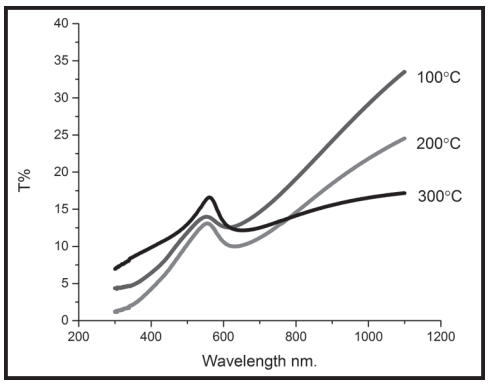

Figure 3: UV-Vis transmittance of Co-sputtered films in 5% O_2.

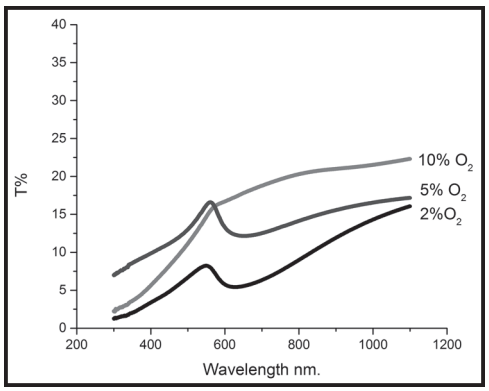

Figure 4: UV-Vis transmittance of Co-sputtered films at 300°C.

EDX was performed on films prepared via co-sputtering at 100-300°C and 5% O_2. Films formed at 100°C and 200°C were shown to have nearly the same relative amounts of Cu and Al. At 300°C, Al content of the film decreased significantly when compared to the Cu content. However, none of the films had the 1:1 Cu:Al ratio necessary for the formation of pure phase $CuAlO_2$.

Conclusions and Future Work:

Ultimately, use of the Cu-Al bilayer structure was proven to be an unviable method of $CuAlO_2$ thin film preparation. Reactive co-sputtering formed films with up to 30% transparency, short of pure phase $CuAlO_2$, but proper characterization of the films would require a crystalline structure. Literature and our preliminary results suggest that $CuAlO_2$ can be formed using this process. Better characterization of the deposition process at various oxygen levels and substrate temperatures will be needed to maintain proper stoichiometric ratios of Cu and Al in order to prepare the $CuAlO_2$ phase.

Possible inclusion of post-deposition annealing will also be tested as a method of ensuring crystalline structure of the films.

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References:

[1] H. Kawazoe, M.Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, Nature 389, 939-942 (30 October 1997).

[2] Nandy, S., Maiti, U.N., Ghosh, C.K., and Chattopadhyay, K.K., "Optical and electrical properties of amorphous $CuAlO_2$ thin film deposited by RF magnetron sputtering," IWPSD 2007. pp.443,445, 16-20 Dec. 2007.