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Effect of Deposition Temperature on the Physical Properties of Ag-Cu_2O Thin Films by D C Magnetron Sputtering

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ABSTRACT
We report co-deposited Ag-Cu_2O films using DC Magnetron Sputtering method on glass substrates. Both Ag content and temperature were varied during deposition. UV-VIS-NIR, Hall measurements were used to characterize the optical and electrical properties. The results reveal that the deposited Ag-Cu_2O films show a decreasing optical transmittance as the content of Ag increases. All the samples that are deposited at room temperature, Ag_2O phase may exist. It is also observed that the resistivity was decreased due to Ag phase formation. The photo-induced conductivity measurement finds highest increase in conductivity by the nature of light irradiation. The co-existence of Ag_2O and Cu_2O was observed in the temperature studies. XRD studies reveal that Ag_2O (002) peaks observed at low temperature and diminished at high temperatures. This study also explains the dissolving of Ag phases into the Cu_2O with the temperature. The reverse effect of formation of Ag phases on Cu_2O was discussed by the method of photoluminescence. The absorption and transmission effect at every Ag percent were understood by optical studies. The conductivity measurements were confirmed by PL measurements. The benefit of Ag-Cu_2O films to be used in optoelectronic related applications were noted in the article.

Keywords **-** DC Magnetron Studies, Ag-Cu_2O thin films, XRD and Optoelectronic Studies

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I. INTRODUCTION

Cuprous oxide (Cu_2O) has been considered as a promising candidate for conceivable applications in photovoltaic appliances [1-3]. It is a reddish p-type semiconductor with a direct forbidden band gap of 2.17 eV, an acceptor level of 0.4 eV above the valence band, and donor levels of 1.1 eV and 1.3 eV below the conduction band. Similarly, it is a known fact that Cu_2O optical transparency is high at the wavelength above 500 nm and high absorption coefficient at the wavelength below 500 nm. Besides non-toxicity and low production cost of Cu_2O films, the theoretical energy conversion efficiency of 20% makes Cu_2O conceivable to be utilized as an absorber layer in thin film heterojunction solar cells [4]. However, the high resistivity of Cu_2O (around 50 Ω cm) would conceivably cause the reduction of photocurrent [5-6]. On the other hand, nanocomposite thin films are attracting more and more interest due to their improved magnetic, mechanical, optical, and electrical properties [7-8]. The addition of silver to the oxide films may induce a significant decrease in their electrical resistivity at room temperature. Pierson et al. studied this effect at room temperature [9] and also Nolan et al. reported the reduction of band gap of Cu_2O due to addition of silver on their work [10]. They also reported the reduction of band gap of Cu_2O and the effect on the conduction properties due to addition of silver particles.

The present study focused co-sputtering process to dope Cu_2O thin films with an amount of Ag particles. This attempt reveals the change of electrical, optical and structural properties due to the temperature. This is a very useful discussion in the light of Cu_2O thin films for optoelectronic related applications.

II. MATERIALS & METHODS

Metallic silver (99.6%) and copper (99.6%) of 2 inches diameter and 2 mm thickness purchased from SISCO India Ltd is used as a sputtering target. All of the Ag-Cu_2O films are deposited on the glass substrate (75mm X 25mm X 1.35mm) obtained from Polar Industrial Corporation, India. The dc reactive magnetron sputtering system developed in the laboratory was used for the preparation of Ag doped Cu_2O thin films. The system was arranged in a sputter down configuration with a substrate to target spacing of 6.5 cm. Cleanliness of the substrate surface, which directly influences the film growth and adhesion, is a prerequisite for the preparation of thin films with reproducible properties. At first the substrates were cleaned ultrasonically for 30 minutes

in the stainless steel tank of the ultrasonic agitation containing trichloroethylene and then washed with distilled water. Thereafter, the substrates were again subjected to ultrasonic agitation for about 15 minutes in isopropyl alcohol and as well as distilled water. Finally, the cleaned substrates were dried by blowing hot air and the substrates along with cleaned stainless steel masks with required geometry were transferred to the sputtering chamber immediately. The chamber was evacuated to an ultimate vacuum of the order of $2X10^{-6}$ mbar using diffusion pump backed by a rotary pump with a liquid argon gas. The presputtering was done for about 30 minutes, before each deposition, for both copper and silver targets in pure argon to remove surface oxide layer formed if any on the target surface during exposure to air. After cleaning the ultimate pressure in the vacuum chamber, pure oxygen gas was admitted into the chamber through the needle valve and the required oxygen partial pressure was set and allowed to stabilize. Argon gas then introduced and the required sputtering pressure was maintained. In this work, the Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer is used to record visual transmittance and absorbance of the films deposited on glass substrates in the wavelength range 300-2000 nm. The Rigaku MiniFlex 600 X-ray diffractometer (XRD) is used for structural analysis of Ag doped Cu_2O thin films. The IR spectra of the Ag doped Cu_2O thin films were recorded on Bruker Alpha- Eco ATR–FTIR (Attenuated total reflection–Fourier transform infrared) interferometer with single reflection sampling module equipped with ZnSe crystal.

III. RESULT AND DISCUSSION

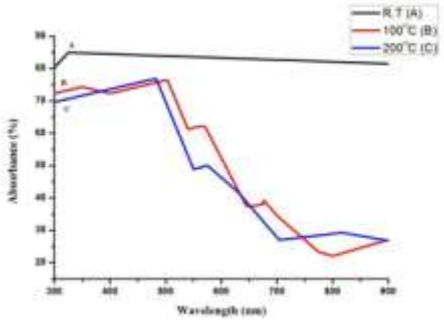

Fig.1: The Temperature effect on Optical Absorbance of Ag doped Cu_2O films.

Fig. 1 describes the effect of absorbance of the deposited films prepared at room temperature, 100°C and 200°C. It is observed that samples significantly show good absorption below 400 nm wavelength. This is due to inherent optical band gap of Cu_2O. Also the absorption edge shift towards right when temperature of the sputtering chamber increased. The behavior is different with room temperature and however at 100°C the absorption coefficient is aligned with available literature [11].

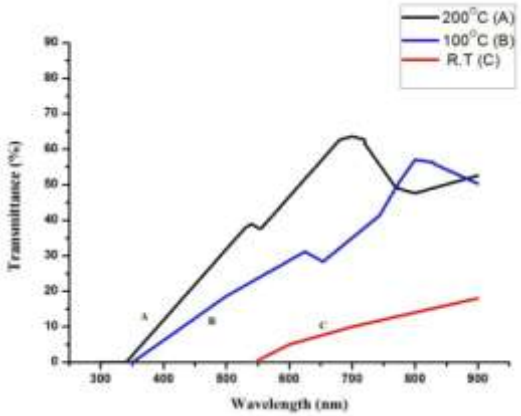

Fig.2: The Temperature effect on Optical Transmittance of Ag doped Cu_2O films.

Fig 2 shows the effect of transmittance at room temperature as well as at different temperatures. The transmittance is decreased with increase of temperature when wavelength is more than 470 nm. However at 100°C temperature, the incident light is either absorbed or reflected. As shown in fig. 2, it is found that all the Cu_2O-Ag thin films have higher absorption than that of original Cu_2O film when the wavelength is longer than 475 nm. It is known that the increased light absorption may be attributed to the creation of electron-hole pairs or atomic vibration or plasmonic effects. If the former behaviour occurs, the photo induced current will certainly increase. It can be stated that the film coating at 100°C has the most oblivious behaviour on the creation of electron-hole pairs, which directly cause the increase in photo induced current. Therefore, the formation of Ag phase can have an opposite effect and Ag can serve as a quick recombination site, which reduces the photo-enhanced current.

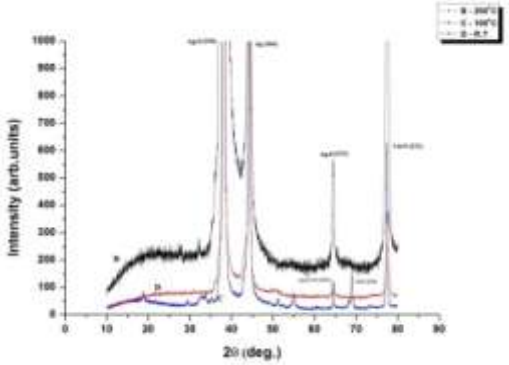

Fig.3: The XRD patterns of Ag doped Cu_2O films at various temperatures.

Fig. 3 shows some of XRD patterns for the film deposited at room temperature, 100°C and 200°C respectively. All the films show a strong

preferred orientation in their respective directions. It is observed that the films at room temperature were distorted with the Ag_2O, Cu_2O and AgO phases and also, the observed planes of Ag_2O, Cu_2O, Ag, CuO and Ag CuO_2 are (200), (222), (200) (220) and (004) respectively. These patterns also show the effect of temperature on the microstructure of the films. However, as shown in fig.3, there are no Ag peaks when the temperature is at 100°C. Indeed, a clear single phase peak is observed at 100°C only. Over that, silver oxide phase still exists when the temperature is higher than 200°C and also the peak overlap with neighbouring strong peaks and not clears. Therefore, the existing peaks and planes are observed only at 100°C. Apparently, secondary phase of Ag plane was formed at the same temperature and the coexistence of Ag_2O and Cu_2O were also observed. The Ag_2O phase is declined at the temperature 200°C. The XRD at 100°C describes that Ag_2O phase is stable and above 100°C it may be unstable and disassociated with oxygen. Under this circumference, silver atoms may be dissolved into the Cu_2O structure and this may need further study.

Fig. 4 shows the FTIR spectrum of Ag doped Cu_2O film. The spectroscopic analysis has revealed that with the increase of temperature, the intensity of characteristic C-H stretching region decreases moderately.

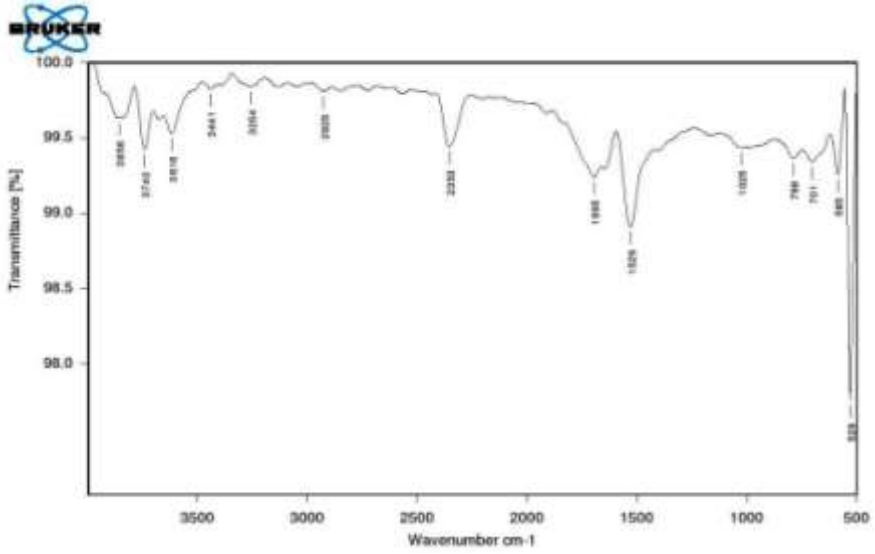

Fig.4: FTIR Spectrum of Ag doped Cu_2O film

The stretching band from the fig 4 assigned to O-H stretch was at 370 nm and medium absorption. The bonds located at 325.4 nm and 292.5 nm have been assigned to C-H vibrational modes and vary with temperature. A weak S-H stretching was at 260 nm observed at room temperature. The other stretches N-O at 152.9 nm and a wide variety of bending vibrations and single band stretches at 529 nm were observed. The C-H stretching was deconvoluted into separate bands corresponding to sp^3 and sp^2 carbon hybridizations. Bands from 280 nm up to 290 nm corresponding to sp^3 carbon and more wave number stands for sp^2 carbon atoms at room temperature only. The sp^3 /sp^2 relation has been estimated by taking the mid areas of the approximating peaks. In all cases, increase in the temperature in DC magnetron sputtering results in favour of sp^2 bonding when compared to sp^3 bond. The results also suggest incorporating of silver in solids into copper lattice was observed at the temperature 200°C. This is one way to understand the absorption coefficient studied by UV method [12]. The FTIR results suggest that an amorphous hydrogenated carbon phase is formed when the temperature is more than 100°C. Similarly at higher temperatures (200°C) the films show an amorphous like structure. These structural changes verses the temperatures are in good agreement with the analysis of electrical properties like resistivity and Hall mobility.

IV. Conclusion

In the present study, Ag doped Cu_2O thin films with different temperature were deposited on glass substrate by the method of DC Magnetron Sputtering. The deposited film's optical transmittance decreased with increasing the temperature and at the temperature 100°C the films are most oblivious behaviour on the creation of electron-hole pair. XRD revealed that the secondary phase of Ag plane was formed at 100°C temperature and the coexistence of Ag_2O and Cu_2O were also observed. FTIR studies revealed the stretching bands that are assigned to O-H, N-H, C-H and S-H stretches. Increase in the temperature in DC magnetron sputtering results in favour of sp^2 bonding when compared to sp^3 bond. Thus, the

structural changes verses the temperatures are in good agreement with the analysis of electrical properties of optoelectronic related applications in the photovoltaic devices.

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