



Optical and electrical properties of *p*-type transparent conducting CuAlO₂ thin film synthesized by reactive radio frequency magnetron sputtering technique

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Abstract : Thin films of *p*-type transparent conducting CuAlO₂ have been synthesized through reactive radio frequency magnetron sputtering on silicon and glass substrates at substrate temperature 300 °C. Reactive sputtering of a target fabricated from Cu and Al powder (1:1.5) was performed in Ar+O₂ atmosphere. The deposition parameters were optimized to obtain phase pure, good quality CuAlO₂ thin films. The films were characterized by studying their structural, morphological, optical and electrical properties.

Keywords : Sputtering; electrical conductivity; optical properties

PACS Nos. : 81.15.Cd; 73.50.-h; 78.66.-w

1. Introduction

In recent years, extensive studies have been carried out on transparent conducting oxide semiconductor materials of both *p*- and *n*-type. It has been found that there are many oxide materials like ZnO [1-3], CdO [4, 5], SnO₂ [6, 7] *etc.* which can serve as a good *n*-type TCO material. Many efforts have been focused on the search for a suitable *p*-type transparent conducting oxide (TCO) material for thin film applications. Different materials like CuO [8, 9], NiO [10, 11] *etc.* show *p*-type conductivity but do not have enough technical advantages either because of low conductivity or for not having sufficiently large band gap to become transparent in the visible region. CuAlO₂ is one of the ideal *p*-type materials which can be employed to prepare thin films with excellent technical ability. Consequently CuAlO₂ thin films can be used in various applications such as in solar cells [12], light emitting diodes, photo transistors *etc.* Different deposition techniques

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have been employed previously to synthesize CuAlO_2 thin film like sol-gel [13], DC sputtering [14, 15], RF sputtering [16] ion exchange technique [17] *etc.* A survey of literature reveals that it requires more than 1200°C [18, 19] to prepare CuAlO_2 , which is a major obstacle to deposit its film in many substrates like glass, polymer *etc.* Keeping this in mind we attempted to prepare CuAlO_2 thin film at lower substrate temperature by reactive RF sputtering. We used RF sputtering technique because this is one of the most useful ways [20] to prepare uniform and high quality thin film. For the synthesis of CuAlO_2 thin films, Kawazoe *et al.* [21] and Yanagi *et al.* [22] used PLD method. However, there are some limitations of the PLD method such as the necessity of costly equipment and the difficulty in scaling-up of the technology. Hence, it is of utmost importance to develop alternative synthesis route of this important material for the full exploitation of its tremendous technological potential.

2. Experimental procedure

2.1 Target preparation and film synthesis :

Target for sputtering was fabricated by taking a mixture of pure Cu and Al powder in 1:1.5 atomic ratios. The mixture was then placed in a grooved aluminum holder of diameter 5 cm and pressed into pellet by a hydrostatic pressure of 100 Kg/cm^2 . The RF sputtering system consists of a conventional vacuum system, which was evacuated to 5×10^{-6} mbar by a combination of a rotary and a diffusion pump. During deposition period of 1 hr the temperature of the substrates were kept fixed at 300°C and chamber pressure at 0.1 mbar. The reactive sputtering process was carried out with a RF power of 200 W and self bias of 250 V. The films were deposited on glass and silicon substrates. The glass substrates were cleaned first by mild soap solution, then washed thoroughly in deionized water and also in boiling water; which were further cleaned ultrasonically for 15 minutes in ethanol. The silicon substrates were immersed in 20% HF solution for five minutes in order to remove the surface oxide layers. Finally, these were washed in deionized water and cleaned by alcohol in an ultrasonic cleaner. The target was pre-sputtered for 15 minutes to remove the surface contamination, if any, and then the shutter was displaced to expose the substrate in the plasma for film deposition.

2.2 Characterization :

X-ray diffraction study (XRD, Bruker, D-8 Advance) was performed for structural characterization using the CuK_α radiation of wavelength ($\lambda = 1.5406\text{\AA}$). The surface morphology of the films was studied by an atomic force microscope (AFM, NT-MDT, Solver Pro) in contact mode. Film thicknesses were measured from the interference fringes of the longer wavelength region of the transmittance spectra. The bonding configuration and the compositional analysis of the films were carried out by X-ray photoelectron spectroscopy (SPECS, Germany) with a hemispherical analyzer (HSA 3500). UV-Vis-NIR spectrophotometric measurements were performed by using a spectrophotometer (Shimadzu UV-3101PC) in the wavelength region of $\lambda = 300 \text{ nm}$ to

900 nm at room temperature. The electrical conductivity was measured by usual four-probe technique using a Keithley electrometer (model 6514).

3. Results and discussion

3.1. Structural and morphological characterization :

The X-ray diffraction pattern of the deposited film is shown in Figure 1. The appeared peaks could be assigned with the delafossite structure of CuAlO_2 . Relatively strong orientation was observed along (006) planes. The surface morphological investigation of the film was performed by atomic force microscopic (AFM) study. The AFM image of the films is shown in Figure 2. The surface has small roughness with an average particle size of 20 nm. The film thickness was measured by cross-sectional SEM image (not shown here) and was found to be 100 nm.

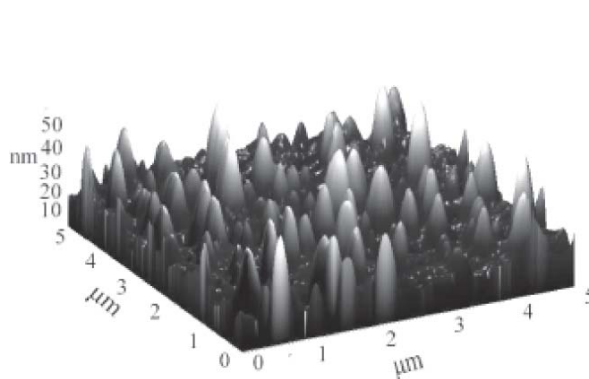
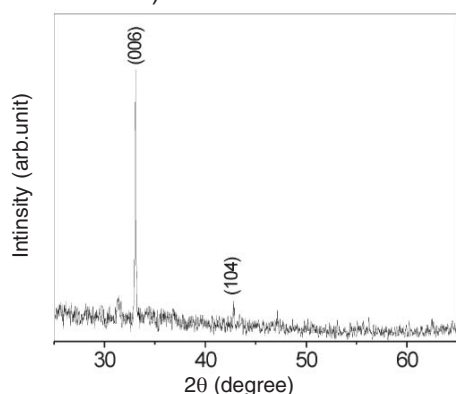


Figure 1. X-ray diffraction pattern of CuAlO_2 thin film. **Figure 2.** AFM image of CuAlO_2 thin film.

3.2 Compositional Analysis :

The bonding configuration and the compositional analysis of the films were carried out by x-ray photoelectron spectroscopic (XPS) measurements. Typical XPS core level spectra of Al and Cu of CuAlO_2 thin film are shown in Figure 3. The binding energies corresponding to Al $2p_{1/2}$, O $1s$ and Cu $2p_{3/2}$ are 73.2 eV, 532 eV and 933.1 eV, respectively which are similar to these reported by Aston *et al* [23].

3.3 Optical characterization :

Transmittance spectrum (shown in Figure 4) of a CuAlO_2 thin film deposited on glass substrate has been used for determining the optical constants of the thin film. The transmittance of CuAlO_2 thin film was found to be more than 70% in the visible region. The transparency is comparable with the published reports both from our group and also with others [14, 24]. The value of the optical band gap can be calculated using the fundamental absorption, which corresponds to electron excitation from the valence band

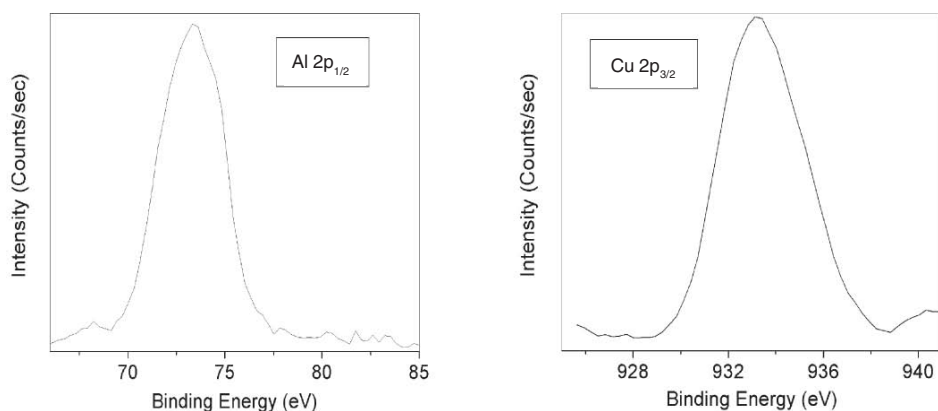


Figure 3. XPS core level spectra of Al and Cu in CuAlO_2 thin film.

to conduction band. The absorption coefficient (α) and the incident photon energy ($h\nu$) are related by the equation [25]

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (1)$$

where A is a constant, E_g is the band gap of the material and the exponent n depends on the type of transition. $n = 1/2, 2, 3/2$ and 3 correspond to allowed direct, allowed indirect, forbidden direct and forbidden indirect respectively. Taking $n = 1/2$, we have calculated the direct optical band gap from $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot (Figure 5) by extrapolating the linear portion of the graph to $h\nu$ axis. The intercept on the $h\nu$ axis determines the direct band gap. The value of the direct band gap has been found to be 3.95 eV for CuAlO_2 . This high band gap is due to quantum confinement effect. For 90 nm particle size the band gap of CuAlO_2 was reported ~ 3.34 eV [26] while here with 20 nm particle size the band gap is obtained as 3.94 eV. A detailed study of quantum confinement effect in band-gap widening for CuAlO_2 has been illustrated in our previous report [26].

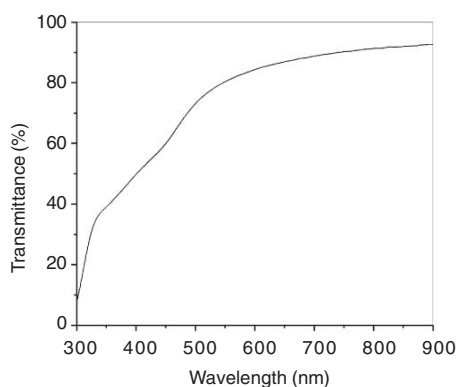


Figure 4. Transmittance spectrum of a CuAlO_2 thin film.

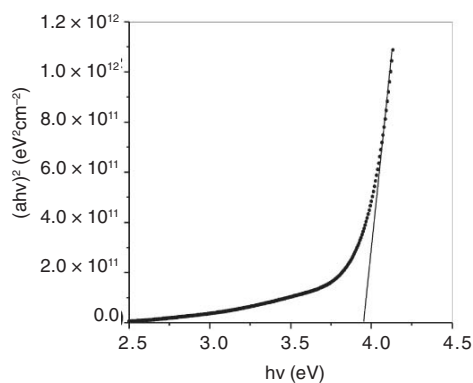


Figure 5. $(\alpha h\nu)^2$ vs. $h\nu$ plot of CuAlO_2 thin film.

3.4 Electrical characterization :

The reactive sputter deposited thin film of CuAlO₂ showed p-type conductivity. The room temperature electrical conductivity of CuAlO₂ thin film was found to be 0.15 Scm⁻¹. The electrical conductivity as obtained in our DC sputtered films was 0.08 S cm⁻¹ [14], while highly conducting CuAlO₂ has been prepared by solution method by Tonooka *et al* [18]. Further doping with external element may improve the transport properties significantly [27]. The cause of p-type conductivity shown by this material is due to metal deficit (or excess oxygen) within the crystallite sites of the material, *i.e.* the defect chemistry plays an important role. This is due to the deviation from the stoichiometric composition of the components, which can be induced by regulating the preparation condition of the material. The approximate defect reaction may be represented by the following equation [28, 29]



where O_O, V_{Cu}, V_{Al}, and h denote the lattice oxygen, Cu vacancy, Al vacancy and hole, respectively. Superscripts 'X', '-' and '+' denote effective neutral, negative and positive charge states, respectively.

4. Conclusions

We have successfully synthesized CuAlO₂ thin film by reactive radio frequency magnetron sputtering technique. The film of CuAlO₂ with excellent crystallinity was prepared by proper optimization of sputtering parameters. The direct band gap of CuAlO₂ thin film was found to be 3.95 eV and films were having good optical transparency of about 70% in the visible range. Electrical conductivity of 0.15 S cm⁻¹ was observed in the film.

Acknowledgment

Two of us (BS & RT) wish to thank the University Grants Commission (UGC) and the Council of Scientific & Industrial Research (CSIR), the Govt. of India, respectively, for awarding them Junior Research Fellowships (JRF) during the execution of the work. The authors also wish to thank the UGC for the UPE scheme and the Department of Science and Technology, Govt. of India, for financial support.

Reference

- [1] H Liu, X Zhang, L Li, Y X Wang, K H Gao, Z Q Li, R K Zheng, S P Ringer, B Zhang and X X Zhang *Appl. Phys. Lett.* **91** 0725111 (2007)
- [2] A Ashida, T Nagata and N Fujimura *J. Appl. Phys.* **99** 013509 (2006)
- [3] L Miao, S Tanemura, M Tanemura, S P Lau and B K Tay *J. Mater. Sci. Mater. Electron* **18** 343 (2007)
- [4] Y Dou, T Fishlock, R G Egdell, D S L Law and G Beamson *Phys. Rev.* **B 55** 13381 (1997)
- [5] B Saha, R Thapa and K. K. Chattopadhyay, *Solid State Commun.* **145** 33 (2008)
- [6] R Djulgerova, L Popova, G Beshkov, Z L Petrovic, Z Racocevic, V Mihailov, V Gencheva and T Dohnalik *J. Phys. D: Appl. Phys.* **39** 3267 (2006)
- [7] H Huang, O K Tan, Y C Lee, M S Tse, J Guo and T White *Nanotechnology* **17** 3668 (2006)

- [8] W T Yao, S H Yu, Y Zhou, J Jiang, Q S Wu and L Zhang *et al*, *J. Phys. Chem. B* **109** 14011 (2005)
- [9] X Wang, G Xi, S Xiong, Y Liu, B Xi, W Yu *et al*, *Cryst. Growth Des.* **7(5)** 930 (2007)
- [10] J M Caruge, J E Halpert, V Bulovic and M G Bawendi *Nano Lett.* **6** 2991 (2006)
- [11] X Wang, L Li, Y Zhang, S Wang, Z Zhang and L Fei *et al*, *Cryst. Growth Des.* **6** 2163 (2006)
- [12] J Bandara and J P Yasomanee *Semicond. Sci. Technol.* **22** 20 (2007)
- [13] Z Deng, X Zhu, R Tao, W Dong and X Fang *Mater. Lett.* **61** 686 (2007)
- [14] A N Banerjee, S Kundoo and K K Chattopadhyay *Thin Solid Films* **440** 5 (2003)
- [15] A N Banerjee, C K Ghosh and K K Chattopadhyay *Solar Energy Mater. Solar Cells* **89** 75 (2005)
- [16] Y M Lu, Y B He, B Yang, A Polity, N Volbers, C Neumann, D Hasselkamp and B K Meyer *Phys. Stat. Sol. (c)* **3** 2895 (2006)
- [17] L Dloczik, Y T Omm, R Konenkamp, M C Lux-Steiner and Th. Dittrich *Thin Solid Films* **451–452** 116 (2004)
- [18] K Tonooka, K Shimokawa and O Nishimura *Thin Solid Films* **411** 129 (2002)
- [19] K Park, K Y Ko and W S Seo *J. European Ceramic Society* **25** 2219 (2005)
- [20] K L Chopra *Thin film Phenomena* (New York : Mc Graw-Hill) ch. 2, p. 23 (1969)
- [21] H Kawazoe, M Yasukawa, H Hyodo, M Kurita, H Yanagi and H Hosono *Nature (London)* **389** 939 (1997)
- [22] H Yanagi, S Inoue, K Ueda, H Kawazoe, H Hosono and N Hamada *J. Appl. Phys.* **88** 4159 (2000)
- [23] D J Aston, D J Payne, A J H Green and R G Egdell *Phys. Rev. B* **72** 1951151 (2005)
- [24] A Sivasankar Reddy, P Sreedhara Reddy, S Uthanna and G Mohan Rao *J. Mater. Sci. Mater. Electron* **17** 615 (2006)
- [25] J I Pankove *Optical Processes in Semiconductors* (Prentice-Hall, Englewood Cliffs) p. 34 (1971)
- [26] A N Banerjee and K K Chattopadhyay *J. Appl. Phys.* **97** 084308 (2005)
- [27] M V Lalic, J Mestnik-Filho, A W Carbonari and R N Saxena *Solid State Communications* **125** 175 (2003)
- [28] P Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, (Canada : Wiley-Interscience) (1972)
- [29] K Koumoto, H Koduka and W S Seo *J. Mater. Chem.* **11** 251 (2001)