Research Article

Optical and Electrical Properties of Magnetron Sputtering Deposited Cu–Al–O Thin Films

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We have successfully prepared Cu–Al–O films on silicon (100) and quartz substrates with copper and aluminum composite target by using radio frequency (RF) magnetron sputtering method. We have related the structural and optical-electrical properties of the films to the sputtering area ratio of Cu/Al for the target ($r_{\text{Cu/Al}}$). The deposition rate of the film and $r_{\text{Cu/Al}}$ can be fitted by an exponential function. $r_{\text{Cu/Al}}$ plays a critical role in the final phase constitution and the preferred growth orientation of the CuAlO₂ phase, thus affecting the film surface morphology significantly. The film with main phase of CuAlO₂ has been obtained with $r_{\text{Cu/Al}}$ of 45%. The films show p-type conductivity. With the increase of $r_{\text{Cu/Al}}$, the electrical resistivity decreases first and afterwards increases again. With $r_{\text{Cu/Al}}$ of 45%, the optimum electrical resistivity of 80 $\Omega \cdot \text{cm}$ is obtained, with the optical transmittance being 72%–79% in the visible region (400–760 nm). The corresponding direct band gap and indirect band gap are estimated to be 3.6 eV and 1.7 eV, respectively.

1. Introduction

Transparent conducting oxide (TCO) films have been widely used in the fields of flat panel displays, solar cells, touch panels, and other optoelectronic devices owing to their high electrical conductivity and optical transmittance in visible region [1–3]. Up to now, however, most of the TCOs obtained are characterized by n-type conductivity. The lack of p-type TCOs restricts the development of p-n junction based device. Therefore, developing stable p-type TCOs becomes the hot research topic [4, 5]. Kawazoe et al. [6] investigated delafossite-structured CuAlO₂ and successfully prepared CuAlO₂ films using pulse laser deposition (PLD) method in 1997. The obtained films are good p-type TCO materials, with room temperature electrical conductivity being 0.095 Scm^{-1} , optical transmittance being 80% and direct band gap being 3.5 eV. Alternatively, Gao et al. [7]

had fabricated p-type transparent CuAlO₂ thin films by spin-on technique and reported the film had a conductivity of 2.4 Scm^{-1} with the optical band gap being 3.75 eV. Due to the excellent optical-electrical properties, CuAlO₂ film is attracts increasing research interest for the potential applications ranging from p-n junction to invisible circuits.

So far, various deposition techniques have been employed to fabricate highly transparent conductive CuAlO₂ thin films, including chemical vapor deposition (CVD) [8], pulsed laser deposition (PLD) [9, 10], sol-gel [11], and sputtering [12, 13]. Among these techniques, RF magnetron sputtering takes the advantage of strong adhesion between film and substrate, large area deposition, low substrate temperature, and good compatibility with current microelectronics. However, various deposition parameters such as oxygen partial pressure, the variety of sputtering target, and sputtering power may influence the

properties of the films. Furthermore, most of the CuAlO_2 films deposited by RF sputtering method are always using high-cost CuAlO_2 ceramic target. In this work, we simplify the preparation process by using the low-cost copper and aluminum composite target instead of CuAlO_2 ceramic target. We investigate the influence of sputtering area ratio of Cu/Al for the target ($r_{\text{Cu/Al}}$) on the properties of obtained films. We elucidate the underlying mechanisms between the film structure and the optical band gap.

2. Experimental

Cu–Al–O films were deposited on silicon (100) and quartz substrates, respectively, by RF magnetron sputtering method at room temperature ($\sim 22^\circ\text{C}$). High purity of 99.999% copper and aluminum composite target was used as the sputtering materials. The composition of the film was controlled by changing the sputtering area ratio $r_{\text{Cu/Al}}$ of Cu and Al for the target. Pure argon and oxygen were used as sputtering gas and reactive gas, respectively. The substrates were cleaned ultrasonically in 5% (volume content) HF, acetone and ethanol for silicon, in acetone, and ethanol for quartz before being loaded into the chamber. The HF solution was stored in closed plastic container, and it was used following the safety rules [14, 15], such as wearing special respirator and gloves to prevent the HF from contacting our skin. Before deposition, base pressure of the chamber was evacuated to 4×10^{-4} Pa by rotary and molecular pump. During deposition process, the working pressure was maintained at 0.3 Pa and sputtering power was fixed at 80 W. We varied the $r_{\text{Cu/Al}}$ over the range 20%–55% to ensure the composition changed from Al being excessive to Cu being excessive. The thickness of the films was controlled being 300 ± 10 nm via the deposition duration time. Before characterized the properties, the samples were annealed in GSL-1400X tubular furnace with argon ambience for 3 h.

The thickness of the films was measured by UVISEL ER wide spectral range Ellipse leaning meter. The structural character was identified by using X'Pert Pro MPD X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm) radiation. The surface morphology and chemical compositions were characterized by ZEISS-SUPRA-55 scanning electron microscope (SEM) and OXFORD INCA PentaFET×3 energy dispersive spectrometer (EDS). An X-ray photoelectron spectroscopy (XPS) apparatus (PHI-5400) was employed to determine the chemical valence of the elements. The conductivity type was identified by HMS-7077 measurement system. Room temperature resistivity of the films was investigated by the four-probe method in Agilent 4155c measurement system. UV-3150 spectrophotometer was used to measure the optical transmittance of the films.

3. Results and Discussion

The deposition rate R_D is one of the most important parameters of the deposition process, which plays an important role in the structure and the properties of the films. It can be obtained through dividing the thickness by deposition time.

Figure 1 illustrates the effect of $r_{\text{Cu/Al}}$ on the deposition rate R_D of the Cu–Al–O films on Si (100) substrate. R_D increases from $1.13 \text{ nm} \cdot \text{min}^{-1}$ to $1.46 \text{ nm} \cdot \text{min}^{-1}$ with the increase of $r_{\text{Cu/Al}}$ from 20% to 55%. The results can be fitted by an exponential function as

$$R_D = 1.5 - 2.3 \exp(-0.1 \cdot r_{\text{Cu/Al}}). \quad (1)$$

The deposition rate R_D increases with the increase of $r_{\text{Cu/Al}}$ is mainly due to that the sputtering yield of Cu is higher than that of Al. In addition, the sputtered Cu atom possesses more energy than Al, thus favoring the formation of defect and nucleation center on the substrate. This also contributes to the increase of R_D .

Figure 2 plots the X-ray diffraction spectra of Cu–Al–O films deposited with different $r_{\text{Cu/Al}}$. When $r_{\text{Cu/Al}}$ is 20%, the diffraction peaks corresponding to CuAlO_2 (104), (015), (009), (116) and Al_2O_3 (113), (306) are observed, indicating an excess of Al element exists in the film. When $r_{\text{Cu/Al}}$ increases to 45%, the CuAlO_2 (018) peak grows remarkably while Al_2O_3 peaks tend to reduce. CuAlO_2 becomes the main phase of the film. The change may be due to the following reaction [16]:

When the $r_{\text{Cu/Al}}$ reaches 55%, a new peak at 36.4° which is identified to Cu_2O (111) emerges, suggesting the surplus of Cu element in the film.

The $r_{\text{Cu/Al}}$ also plays an important role in the preferred growth orientation of CuAlO_2 diffraction peaks. As seen from Figure 2, with $r_{\text{Cu/Al}}$ of 20%, CuAlO_2 phase shows strong peak along (104) and (015) crystal planes, while the X-ray diffraction peak of (018) is weak. With $r_{\text{Cu/Al}}$ increases to 45%, the peak of CuAlO_2 (018) increases significantly and becomes the strongest, suggesting that the preferred growth orientation of CuAlO_2 is (018) with this $r_{\text{Cu/Al}}$. When the $r_{\text{Cu/Al}}$ is 55%, (018) peak of CuAlO_2 weakens and the preferential growth changes into (104). Although the surface energy of (001) crystal plane might be the lowest in delfossite structure CuAlO_2 crystal, the kinetic parameters, for instance, annealing treatment, may also play a role in the selection of the preferred growth orientation.

The grain size can be estimated from the full-width half-maximum intensity of XRD peak by using Scherrer's relation [17]:

$$d = \frac{k\lambda}{\beta \cos \theta}, \quad (3)$$

where k is a constant of 0.89 for Cu target, $\lambda = 0.15406$ nm, θ and β are the Bragg diffraction angle and half intensity width. The calculated grain sizes of the films are estimated to be 12.6 nm, 14.1 nm, 17.4 nm, and 15.2 nm for $r_{\text{Cu/Al}}$ of 20%, 30%, 45%, and 55%, respectively.

Figure 3 displays the typical SEM images and the corresponding EDS spectra of the films deposited with different $r_{\text{Cu/Al}}$ on Si (100) substrate. With $r_{\text{Cu/Al}}$ being 20%, a large amount of globular precipitation phases have been observed, as shown in Figure 3(a). Figure 3(b) illustrates the

FIGURE 1: Deposition rate R_D of the films as a function of sputtering area ratio of Cu/Al for sputtering target ($r_{\text{Cu/Al}}$).

EDS spectrum of the globular phases, showing the atomic ratio of Al:O is around 2 : 3. This suggests that the globular phase is Al_2O_3 . Figure 3(c) demonstrates the image of the film deposited with $r_{\text{Cu/Al}}$ being 45%. The film shows a uniform microstructure with well-defined grain boundaries, no impurity is observed. EDS spectrum of the film signifies the atomic ratio of Cu:Al:O is about 1 : 1 : 2, confirming the XRD analysis that CuAlO_2 is the main phase of the film. When the $r_{\text{Cu/Al}}$ increases to 55%, a nonfaceted phase is observed. EDS analysis of this phase shows that the atomic ratio of Cu:Al:O is about 12 : 1 : 5, indicating the precipitation phase is mainly composed of copper oxide, which is consistent with the XRD result.

To further identify the chemical compositions and valences of the elements, we performed XPS analysis to the films deposited on Si (100) substrate. Figures 4(a)–4(c) show the typical XPS spectra of the Cu–Al–O film obtained with $r_{\text{Cu/Al}} = 45\%$ after the calibration using C 1s position of carbon. As shown in Figure 4(a), the “shake-up” peak of the $\text{Cu}^{2+}2p_{3/2}$ at around 943 eV is not observed, indicating that no Cu^{2+} presents in the film. Figure 4(b) shows the Cu $2p_{3/2}$ peak together with the two separated peaks by using the multi-peaks fitting. The peak at the low binding energy of 931.7 eV is corresponding to Cu^+ in CuAlO_2 , while the high binding energy 932.8 eV is corresponding to Cu_2O . The intensity of the low-energy peak (931.7 eV) is remarkably higher than that of the high-energy peak (932.8 eV), suggesting Cu^+ mainly exists in CuAlO_2 phase. The Al 2p peak region, shown in Figure 4(c), consists of Al 2p peak of Al^{3+} (around 74.2 eV), Cu $3p_{3/2}$ (around 75.3 eV), and Cu $3p_{1/2}$ (77.1 eV) peaks of Cu^+ , which is similar to the result reported by Cai et al. [16].

The Cu 2p spectra of the other films are similar to that shown in Figure 4(a) where no Cu^{2+} peaks have been observed. This is consistent with the XRD results: no CuO or CuAl_2O_4 diffraction peak is observed in the XRD patterns.

FIGURE 2: XRD patterns of Cu–Al–O thin films deposited with different $r_{\text{Cu/Al}}$ on Si (100) substrate.

The conductivity type of the films deposited on quartz substrate was measured by Hall effect measurement and the electrical resistivity (ρ) at room temperature was studied by four-probe method. Prior to the investigation, four Au electrodes were deposited on the film surface.

Figure 5 shows the electrical resistivity (ρ) of the films formed with different $r_{\text{Cu/Al}}$ and the inset demonstrates the relation between current and voltage for the film deposited with $r_{\text{Cu/Al}}$ of 45%. From the inset I - V curve, it can be seen the linear dependence is obtained, which indicates ohmic contact has been achieved between Au electrode and the film. With $r_{\text{Cu/Al}}$ being 20%, the sample shows a high electrical resistivity due to the existence of large amount of insulating Al_2O_3 in the film [18]. When $r_{\text{Cu/Al}}$ increases from 20% to 45%, the electrical resistivity (ρ) decreases from $243 \Omega \cdot \text{cm}$ to $80 \Omega \cdot \text{cm}$. The reason may be that the improvement of crystallization quality reduces the scattering and trapping of charge carriers, leading to the enhancement of Hall mobility. Furthermore, the increment of CuAlO_2 increases the carrier concentration of the film. With $r_{\text{Cu/Al}}$ being 55%, the electrical resistivity (ρ) increases to $156 \Omega \cdot \text{cm}$. In this case, surplus copper element exists in the film and the copper vacancy which can produce hole carrier concentration decreases. In addition, the emergence of Cu_2O impurity strengthens the scattering and trapping of charge carriers, decreasing the Hall mobility.

Figure 6 presents the optical transmittance spectra of the Cu–Al–O thin films deposited with different $r_{\text{Cu/Al}}$ on quartz substrate. As can be seen, the film deposited with $r_{\text{Cu/Al}}$ of 20% exhibits the highest transmittance (77%–84%) in the visible region (400–760 nm). It may be due to the large amount of Al_2O_3 precipitation phase, which has quite high transmittance in the visible range, existing in the film. With $r_{\text{Cu/Al}}$ being 30%, a decrease (58%–76%) in the film transmittance was observed. When $r_{\text{Cu/Al}}$ increases to 45%,

FIGURE 3: SEM micrographs and EDS spectra of Cu–Al–O thin films obtained with different $r_{\text{Cu/Al}}$: (a) and (b) $r_{\text{Cu/Al}} = 20\%$; (c) and (d) $r_{\text{Cu/Al}} = 45\%$; (e) and (f) $r_{\text{Cu/Al}} = 55\%$.

the transmittance of the film increases to 72%–79% in the visible region (400–760 nm) due to that the CuAlO_2 becomes the predominant phase. In addition, the decrease of defect density and crystallization improvement of the films also contribute to the improvement of optical transmittance. When $r_{\text{Cu/Al}}$ reaches 55%, the transmittance decreases again, mainly because the coexistence of Cu_2O phase strengthen the scattering effect, lowering the optical transmittance [18].

To further investigate the optical properties, we evaluated the optical band gap (E_g) of the Cu–Al–O thin films. The optical absorption coefficient (α) of the films can be calculated using the following equation:

$$\alpha = \frac{1}{d} \ln\left(\frac{1}{T}\right), \quad (4)$$

FIGURE 4: XPS spectra of Cu–Al–O thin films obtained with $r_{\text{Cu/Al}}$ of 45%: (a) Cu 2p spectra; (b) fitting spectra of Cu 2p_{3/2}; (c) fitting spectra of Al 2p and Cu 3p.

where d is the film thickness and T is the transmittance of the film. The relation between optical absorption coefficient (α) and optical band gap (E_g) can be written as

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g), \quad (5)$$

where A is the absorption edge width parameter and $h\nu$ means the incident photon energy. The exponential n is 1/2 or 2 for direct allowed transition (E_{gd}) or indirect allowed transition (E_{gi}).

Figure 7 shows a typical linear fitting process of E_g for the Cu–Al–O thin film deposited at $r_{\text{Cu/Al}} = 45\%$. E_{gd} and E_{gi} are obtained from the intercept on $h\nu$ axis in the plots of $(\alpha h\nu)^2 - h\nu$ and $(\alpha h\nu)^{1/2} - h\nu$, respectively. Figure 8 compares the E_{gd} and E_{gi} values of the films deposited with different $r_{\text{Cu/Al}}$. The E_{gd} decreases from 5.3 eV to 3.6 eV with increase of $r_{\text{Cu/Al}}$ from 20% to 45%, afterwards, it increases to 4.7 eV

FIGURE 5: Variation of electrical resistivity with different $r_{\text{Cu/Al}}$. Inset shows the I - V relation for the sample deposited with $r_{\text{Cu/Al}}$ of 45%.

FIGURE 6: Optical transmittance spectra of Cu–Al–O films deposited with different $r_{\text{Cu/Al}}$.

with $r_{\text{Cu/Al}}$ reaching 55%. E_{gi} varies in the range of 1.6–1.9 eV and achieves the minimum with $r_{\text{Cu/Al}}$ of 45%.

E_{gd} and E_{gi} may be influenced by the phase constitution of the films. With $r_{\text{Cu/Al}}$ of 20%, the film is composed of Al₂O₃ and CuAlO₂ phases, hence, the optical band gap of the film can be evaluated by the superposition of pure Al₂O₃ and CuAlO₂, whose E_{gd} are 9.0 eV [19] and 3.5 eV [6, 20], respectively. The direct band gap of the film which consists of Al₂O₃ and CuAlO₂ is assumed to be in the range of 3.5–9.0 eV. This is in agreement with our result 5.3 eV. For the film deposited with $r_{\text{Cu/Al}}$ of 45%, the main crystal phase of the film is CuAlO₂ and the estimated E_{gd} (3.6 eV) is close to the E_{gd} of pure CuAlO₂ (3.5 eV) [6, 20].

FIGURE 7: Plots of $(\alpha h\nu)^2$ versus $h\nu$ for the determination of direct band gap (E_{gd}) for the film deposited with $r_{Cu/Al}$ of 45% (inset: determination of indirect band gap E_{gi}).

FIGURE 8: Effect of $r_{Cu/Al}$ on the optical band gap of the film: (a) direct band gap E_{gd} ; (b) indirect band gap E_{gi} .

Moreover, quantum size effect may also affect the band gap, which can be described by the following equation [20]:

$$E_g = \frac{\pi^2 \hbar^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon_2 R} + \frac{e^2}{R} \sum_{n=1}^{\infty} \alpha_n \left(\frac{S}{R} \right)^{2n}, \quad (6)$$

R is the radius of the semiconductor particle and the first term is the quantum energy of localization for both electron and hole. The second term is the Coulomb attraction and the third term represents the band gap of the bulk semiconductor. As is shown in the model, the change tendency of E_g and R is reverse, that is, E_g should be smaller for larger R . The estimated results show that with the largest grain size 17.4 nm ($r_{Cu/Al} = 45\%$), the E_{gd} achieves the minimum value 3.6 eV, while with the minimum grain size 12.6 nm ($r_{Cu/Al} = 20\%$), the E_{gd} obtains the maximum value

5.3 eV, indicating our results is consistent with the model. This suggests that quantum size effect resulted from the nano size grain structure may play a role in the optical band gap of the film.

4. Conclusions

Cu–Al–O thin films have been deposited on Si (100) and quartz substrates by RF magnetron sputtering technique. The sputtering area ratio of Cu/Al for the sputtering target ($r_{Cu/Al}$) plays an important role in the structure, optical-electrical properties and optical band gaps of the films. The deposition rate R_D increases with the increase of $r_{Cu/Al}$ mainly because of the higher sputtering yield of Cu than Al. With $r_{Cu/Al}$ of 20%, $CuAlO_2$ and Al_2O_3 phases coexist in the film due to the surplus Al element. $CuAlO_2$ becomes the main phase of the film when $r_{Cu/Al}$ reaches 45%. Whereas when $r_{Cu/Al}$ increases to 55%, as well as the $CuAlO_2$, Cu_2O diffraction peak also be detected. Cu^+ in the films deposited with different $r_{Cu/Al}$ exists in the form of $CuAlO_2$ or Cu_2O , no Cu^{2+} has been observed. The films show stable p-type conductivity. With the increase of $r_{Cu/Al}$, the electrical resistivity first decreases afterwards increases. With $r_{Cu/Al}$ of 45%, the film shows the optimum optical-electrical properties. The electrical resistivity is measured to be $80 \Omega \cdot cm$ with the transmittance being 72%–79% in the visible region (400–760 nm). The estimated E_{gd} is in the range of 3.6–5.3 eV and E_{gi} in the range of 1.6–1.9 eV which depends on $r_{Cu/Al}$.

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