Abstract: Cu\textsubscript{2}O thin film has been widely studied due to its intrinsic \textit{p}-type conductivity. It can be used as \textit{p}-type transparent conductive electrode or hole transport layer in various potential applications. However, its intrinsic \textit{p}-type conductivity is very limited, which needs to be optimized by introducing acceptor defects. In this work, the electrical properties of the Cu\textsubscript{2}O films was improved through introducing interstitial oxygen in the films those were deposited via direct current sputtering assisted by oxygen ion beam. The results show that with oxygen ion beam current increase, the carrier concentration effectively improves. However, with more interstitial oxygen introduced, the film’s crystallinity significantly reduces, as well as the carrier mobility decreases. Meanwhile, all of the Cu\textsubscript{2}O films present moderate transmittance in the visible region (400–800 nm), but ideal transmittance in the near infrared (NIR) light region (800–2500 nm). When compared with the strong reflection of the \textit{n}-type transparent conductive film to the near infrared light, the Cu\textsubscript{2}O film is transparent conductive in NIR region, which expands its application in the fabrication of NIR electrical devices.

Keywords: \textit{p}-type conductivity; Cu\textsubscript{2}O film; vis-NIR region; reactive sputtering; optoelectronic property

1. Introduction

The transparent conductive oxides (TCOs) combined high optical transmittance and ideal electrical conductivity are widely used in various fields, for example, flat panel displays, touch screens, transparent electrodes, and so on [1–3]. However, the currently widely used TCO are mostly \textit{n}-type semiconductors, such as SnO\textsubscript{2}:F (FTO), In\textsubscript{2}O\textsubscript{3}:Sn (ITO), ZnO:In,Ga (IGZO), etc. [4–6]. Their transmittance in the visible region can reach more than 85%, while their conductivity can achieve $10^3$ S cm\(^{-1}\), which satisfy the above mentioned application requirements well. However, in the near infrared (NIR) region (800–2500 nm), the transmittance of these \textit{n}-type TCOs drops sharply [7,8]. For instance, the transmittance of ITO decreases rapidly beyond 1200 nm, although its band gap is higher than 3.0 eV [9]. This severely restricts the application of transparent conductive materials in
the NIR region, such as in infrared detection, infrared imaging, and infrared guidance system, etc. In addition, in the photovoltaic field, the current used transparent electrodes on the surface of the solar cell generally possess high transmittance in visible light region, but they have a dramatically deteriorated transmittance in NIR light region. This behavior results in that the NIR light (~50% solar power) cannot be effectively used. Therefore, improving the transmittance of TCO material in the NIR region is full of significance for developing novel optoelectronic devices.

The transmittance of TCOs in NIR region is related to their plasma wavelength ($\lambda_p$), which can be calculated according to the Drude model [10]:

$$\lambda_p = \frac{2\pi C}{\varepsilon_0 \varepsilon_{\infty} m^* c^2 N_m}^{1/2}$$

(1)

where $C$ is the velocity of light, $\varepsilon_0$ and $\varepsilon_{\infty}$ are the permittivity of free space and the high-frequency permittivity, respectively. $m^*$ is the conductivity effective mass, $e$ is the electron charge, and $N_m$ is the carrier concentration. As the model predicted, with the carrier concentration increase or the conductivity effective mass decreases, the plasma wavelength $\lambda_p$ shifts to the shorter wavelength. As in $n$-type TCOs, the conductivity effective mass is normally below 0.4 $m_e$, while their carrier concentration is very high and even presents degenerate characteristics [11–13]. Thus, the plasma wavelength of $n$-type TCO normally falls in the NIR region, and $n$-type TCOs possess poor transmittance in this region.

Cu-based oxides have recently attracted increasing attention [14–16]. The band gap of intrinsic $p$-type Cu$_2$O is about 2.4–2.8 eV, allowing for part of visible light to pass through [17,18]. At the same time, its conductivity effective mass of about 0.7 $m_e$ is much higher than that of the traditional $n$-type TCOs [19]. Therefore, its plasma wavelength can still fall in mid-infrared or even far-infrared region, even if a higher carrier concentration is achieved. As a result, Cu$_2$O exhibits excellent light transmittance in the NIR region. In addition, the simple structure, non-toxic, and stable characteristics make Cu$_2$O suitable to be used in various applications [20,21]. Indeed, it is an ideal vis-NIR transparent conductive material.

In the current work, the Cu$_2$O films were deposited by magnetron sputtering technique under oxygen-rich conditions. Oxygen ion beam was employed during the deposition process, so as to improve the oxygen amount in the films, thereby increasing the acceptor defects concentration, and further enhancing the film’s electrical performance. The influence of the oxygen ion beam current on the structure and optoelectronic properties of Cu$_2$O films was discussed in detail. Subsequently, a transparent conductive Cu$_2$O film in vis-NIR region can be realized through optimizing the deposition parameters.

2. Materials and Methods

Cu$_2$O films with a thickness within 420–450 nm were deposited on glass substrates from pure copper targets (purity 99.99%) by reactive magnetron sputtering with DC power supply at room temperature. The oxygen ion source was used to assist the deposition process in order to improve the oxygen amount in the films. The oxygen ion beam current ($I_{O_2}$) is varied (0–5.0 A) to adjust the oxygen amount in the films. Before the deposition, the background of the reactive chamber was pre-pumped to $10^{-5}$ Pa. Subsequently, the gas mixture of Ar + O$_2$ was introduced into the chamber. The oxygen flow ratio is fixed at 10%, while the gas flow rates of Ar and O$_2$ are 180 sccm and 20 sccm, respectively. The working pressure is fixed at 1.0 Pa. During the deposition, the pulsed frequency of the power supply was fixed at 50 kHz, while the pulse off-time maintains at 5 µs. The deposition process maintains 15 min. After the deposition, all of the films were annealed at 423 K for 20 min in air ambient.

The film’s thickness was determined by surface profilometer (Ambios Technology Company, Santa Cruz, NM, USA). Energy-dispersive spectroscopy confirmed the film’s composition (EDS, Nova Nano SEM 450, Hillsboro, OR, USA). The phase structures were investigated by X-ray diffractometer (XRD,
Rigaku Ultima IV, Rigaku, Tokyo, Japan). The film’s top surface morphology was observed by scanning electron microscope (SEM, Nova Nano SEM 450, Hillsboro, OR, USA). Hall effect analysis with van der Pauw’s configuration (Keithley-4200 SCS, Beaverton, OR, USA) was used in order to analyze the film’s electrical properties. The film’s optical properties in the visible region and NIR region were characterized by UV-Vis-NIR spectrophotometer (PerkinElmer LAMBDA 1050, Waltham, MA, USA).

3. Results and Discussion

Figure 1 illustrates the evolution of the film’s composition as oxygen ion beam current ($I_{O_2}$) increase. It is demonstrated that the film deposited under Ar + O$_2$ ambience without oxygen ion beam assisted is O-deficient. For the films deposited with oxygen ion beam assisted, the oxygen amount in the films gradually increases, until the film is oxygen-rich. For Cu$_2$O film, the intrinsic acceptor defects are copper vacancies or interstitial oxygen [22,23]. Thus, oxygen-rich condition is beneficial for fabricating Cu$_2$O film with higher interstitial oxygen concentration, and further enhancing the film’s p-type conductivity.

![Figure 1](image)

Figure 1. The atomic ratio of Cu$_2$O films deposited with various oxygen ion beam current.

Figure 2 compares the phase structural properties of Cu$_2$O films deposited with various $I_{O_2}$. It can be observed that all of the films are crystallized in Cu$_2$O structure (JCPDS: 77-0199). No impurity phase can be detected here. The diffraction peaks at 36.5°, 42.4°, 61.6°, and 73.7° correspond to the (006), (101), (012), and (104) orientations, respectively. With $I_{O_2}$ increase, the crystallinity of Cu$_2$O films degrades. It is due to that more interstitial oxygen are introduced into Cu$_2$O films, which arises the lattice distortion and reduces the film’s crystallinity. Meanwhile, as $I_{O_2}$ increases, the inserted interstitial oxygen leads to an increment in the lattice parameter and it results in compressive stresses in the films, thus the diffraction peaks gradually shift to the lower angle [21].

SEM micrographs of the top surface for Cu$_2$O films that were deposited with various oxygen ion beam current on glass substrate are shown in Figure 3. With increase in the oxygen ion beam current, the surface particles change from spheroid to interconnected dendritic shape. We speculate that, in the case of higher oxygen ion beam current, oxygen ion beam with higher energy arrivals the film surface, bombarding the incident Cu atoms and allowing them to migrate on the film’s surface. This behaviour promotes the connection between the neighboring Cu$_2$O particles and causes the film’s growth mode changing from island growth to layer-by-layer growth. In addition, as the oxygen ion beam current above 4.0 A, some cracks appeared on the surface of the films. This might be caused by that the residual stress existed in the film under high oxygen ion beam current condition, as mentioned in XRD analysis.

Figure 4 shows the film’s electrical properties as a function of $I_{O_2}$. The film deposited under Ar + O$_2$ ambience without oxygen ion beam assisted is insulant, while its carrier concentration and carrier mobility cannot be detected by our instrument. As for the films deposited with oxygen ion beam assisted, their electrical properties are greatly enhanced. All of them present p-type conductivity. With $I_{O_2}$ increase, the film’s conductivity first significantly increases from 7.3 × 10$^{-3}$ S·cm$^{-1}$ ($I_{O_2}$ = 1.3 A) to
the optimal value of $1.1 \times 10^{-1}$ S·cm$^{-1}$ ($I_{O_2} = 3.0$ A), and then decrease to $9.0 \times 10^{-3}$ S·cm$^{-1}$ ($I_{O_2} = 5.0$ A) (Figure 4a). This behaviour is affected by the variation of the carrier concentration and the carrier mobility (Figure 4b). With an increase in $I_{O_2}$, more interstitial oxygen defects are introduced into Cu$_2$O films, as shown in Figure 4b. Interstitial oxygen is the main acceptor defects in Cu$_2$O, as reported by Nolan et al. [23]. Consequently, the carrier concentration effectively improved. However, when $I_{O_2}$ reaches 3.0 A, the concentration of interstitial oxygen tends to be saturated in Cu$_2$O film, and the carrier concentration increased slightly with $I_{O_2}$ rising. Meanwhile, the carrier mobility reduces with increase in the oxygen ion beam current. It is primarily determined by the crystallinity of the film. With more interstitial oxygen being introduced into Cu$_2$O film, the grain growth is impeded, and the film’s crystallinity reduces significantly. The finer grains result in a large number of grain boundaries, which hinder the migration of the carriers. Consequently, the carrier concentration drops.

![Figure 2. The X-ray diffractometer (XRD) patterns of Cu$_2$O films deposited with various oxygen ion beam current.](image)

Figure 5 shows the variation in transmittance of Cu$_2$O films deposited with different oxygen ion beam current. As $I_{O_2}$ rises from 0 to 5.0 A, the film’s transmittance gradually reduces both in the visible region and the NIR region. The average transmittance of Cu$_2$O film in the visible region (400–800 nm) and in the NIR region (800–2500 nm) are compared in the inset table. It is calculated from the following Equation [24]:

$$T_{average} = \frac{\int_{\lambda_1}^{\lambda_n} T(\lambda) d\lambda}{\lambda_n - \lambda_1} \approx \frac{1}{m} \sum_{\lambda = \lambda_1}^{\lambda = \lambda_n} T(\lambda) \ (m = \lambda_1, \lambda_2, \ldots, \lambda_n) \quad (2)$$

where $\lambda_1 = 400$ nm and $\lambda_n = 800$ nm for the visible region, and $\lambda_1 = 800$ nm and $\lambda_n = 2500$ nm for the NIR region. It should be noted that the thickness of Cu$_2$O film in the current work is between 420 to 450 nm, which is much thicker than other works [25,26]. Thus, the film’s transmittance can be further improved by reducing the film’s thickness. Additionally, all of the films are highly transparent in NIR region. Especially, as $I_{O_2}$ is 0 A, this value is near 90%. Even when $I_{O_2}$ increases to 5.0 A, the film’s transmittance reduces, its value can also maintain above 70%. This result is far superior to n-type TCO. It makes Cu$_2$O film full of potential to fabricate transparent conductive devices in the NIR region.

The film’s absorption coefficient $\alpha$ can be calculated from the film’s transmittance and reflectance (not given here) by the follow Equation [27]:

$$\alpha = \frac{1}{d} \ln\left(\frac{1-R}{T}\right) \quad (3)$$

where $d$ is the film’s thickness, $R$ and $T$ are the reflectance and transmittance, respectively. Figure 6 shows the absorption coefficient of Cu$_2$O films versus the oxygen ion beam current. It can be seen that all the films present strong absorption in visible region compared in NIR region. The variation of the
absorption coefficient exhibits a reverse trend with respect to the film's transmittance. In addition, the optical absorption edge of Cu$_2$O films deposited with higher $I_{O_2}$ shifts to longer wavelengths, indicating the decrement of the film's band gap.

Figure 3. Scanning electron microscope (SEM) observations the top surface of Cu$_2$O films deposited with various oxygen ion beam current: (a) 0 A, (b) 1.3 A, (c) 2.0 A, (d) 3.0 A, (e) 4.0 A, and (f) 5.0 A.
Figure 4. The (a) conductivity and (b) carrier concentration and carrier mobility of Cu₂O films as a function of oxygen ion beam current.

Figure 5. The transmittance of Cu₂O films deposited with various oxygen ion beam current (the inset table compares the film’s average transmittance in visible region (400–800 nm) and in NIR region (800–2500 nm)).
The film’s band gap $E_g$ can be derived by the following formula [28]:

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

where $h \nu$ is the incident photon energy, $A$ is a constant. The exponent $n$ depends on the type of transition: $n$ equals 2 and 1/2 for indirect and direct transition, respectively. $n$ equals to 1/2 in this Equation since Cu$_2$O has a direct band gap transition. Subsequently, the direct band gap of Cu$_2$O films can be evaluated by a plot of $(\alpha h \nu)^2$ versus $h \nu$. Figure 7 depicts the variation of the direct band gap of Cu$_2$O film deposited with various $I_{O_2}$ value. The band gap of Cu$_2$O films narrows from 2.58 to 2.50 eV with $I_{O_2}$ increasing from 0 to 5.0 A, as shown in this figure. This behavior is affected by the film’s degraded crystallinity. The impurity energy level introduced by the increased defects enhances the absorption of visible light, which, in turn, causes the band gap reduction.

![Figure 6](image-url)  
**Figure 6.** The absorption spectra of Cu$_2$O films deposited with various oxygen ion beam current.

![Figure 7](image-url)  
**Figure 7.** The variation of the direct band gap of Cu$_2$O films.
4. Conclusions

The Cu$_2$O films were deposited by reactive magnetron sputtering under Ar + O$_2$ atmosphere. In order to improve the oxygen content in the films, oxygen ion beam was employed to assist the deposition process, which can further enhance the film’s electrical conductivity. With the oxygen ion beam current (I$_{O_2}$) increase, the crystallinity of Cu$_2$O film degrades. This is primarily due to more defects of interstitial oxygen being introduced into the film. At the same time, the carrier concentration improves, while the carrier mobility decreases. Under the combine effect of the carrier mobility and carrier concentration, the optimal $p$-type conductivity of about $1.1 \times 10^{-1}$ S·cm$^{-1}$ is achieved as I$_{O_2}$ value is 3.0 A. In addition, Cu$_2$O films show moderate transmittance in the visible light region, but they present ideal light transmittance in the near infrared (NIR) region. Its band gap narrows with I$_{O_2}$ increase. The current work depicts the great potential of Cu$_2$O as a transparent conductive material employed in NIR applications since Cu$_2$O film possesses high transmittance in NIR region.

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