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Characterizations of Cupric Oxide Thin Films on Glass and Silicon Substrates by Radio Frequency Magnetron Sputtering

(Pencirian Kuprik Oksida Filem Nipis atas Substrat Kaca dan Silikon dengan Percikan Pemagnetan Frekuensi Radio)

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ABSTRACT

Cupric oxide (CuO) thin films were prepared on a glass and silicon (Si) substrates by radio frequency magnetron sputtering system. The structural, optical and electrical properties of CuO films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), Fourier transform infrared spectrometer, ultra-violet visible spectrophotometer, respectively, four point probe techniques and Keithley 4200 semiconductor characterization system. The XRD result showed that single phase CuO thin films with monoclinic structure were obtained. AFM showed well organized nano-pillar morphology with root mean square surface roughness for CuO thin films on glass and Si substrates were 3.64 and 1.91 nm, respectively. Infrared reflectance spectra shown a single reflection peak which is corresponding to CuO optical phonon mode and it confirmed that only existence of CuO composition on both substrates. The optical direct band gap energy of the CuO film grown on glass substrate, which is calculated from the optical transmission measurement was 1.37 eV. Finally, it was found that the deposited CuO films are resistive and the palladium formed ohmic contact for CuO on glass and schottky contact for CuO on Si.

Keywords: Cupric oxide; radio frequency magnetron sputtering; ultra-violet visible spectroscopy; X-ray diffraction

ABSTRAK

Filem nipis kuprik oksida (CuO) telah disediakan pada substrat kaca dan silikon (Si) dengan sistem percikan pemagnetan frekuensi radio. Struktur sifat optik dan elektrik filem CuO dicirikan masing-masing oleh pembelauan sinar-X (XRD), mikroskopi daya atom (AFM), transformasi Fourier inframerah spektrometer, spektrofotometer ultra-ungu tampak, teknik empat titik penduga dan Keithley 4200 sistem pencirian semikonduktor. Keputusan XRD menunjukkan bahawa fasa tunggal CuO filem nipis dengan struktur monoklinik telah diperoleh. AFM menunjukkan nano tunggak morfologi terancang dengan punca min kuasa dua yang rendah kekasaran permukaan bagi CuO filem nipis atas kaca dan Si masing-masing sebanyak 3.64 dan 1.91 nm. Spektrum pantulan inframerah menunjukkan puncak refleksi tunggal yang sepadan dengan mod fonon optik CuO dan ia mengesahkan bahawa hanya komposisi CuO wujud bagi kedua-dua substrat. Jurang langsung tenaga jalur optik filem CuO, yang dikira daripada pengukuran transmisi optik, adalah 1.37 eV. Akhirnya, didapati CuO filem adalah berintangan dan Pd membentuk sentuhan ohmik bagi CuO atas kaca dan sentuhan schottky bagi CuO atas Si.

Kata kunci: Kuprik oksida; pembelauan sinar-X; percikan pemagnetan frekuensi radio; spektrofotometer ultra-ungu tampak

INTRODUCTION

Copper (II) oxide (CuO) or known as cupric oxide has a preferred monoclinic tenorite structure. Generally, CuO is a p-type transition metal oxide semiconductor due to copper vacancies are the most stable defects in both Cu-rich and O-rich environments (Wu et al. 2006). The band gap of the CuO is in the range of 1.2-2.0 eV (Balamurugan & Mehta 2001; Ogwu et al. 2005; Serin et al. 2005). However, its values are strongly dependent on the grown methods. Apart from that, it is reported that the CuO possess a direct band gap (Balamurugan & Mehta 2001; Maruyama 1998; Ogwu et al. 2005; Oral et al. 2004; Pierson et al. 2003; Ray 2001; Serin et al. 2005, 2011) as well an indirect band gap (Shanid & Khadar 2008; Wu et al. 2006). This is mostly due to the complicated crystal structure and it may belong to that particular class of compounds known as Mott insulators, where conventional band theory generally is failed (Ching et al. 1989).

Over the last few decades, non-toxic and abundance CuO has undergone intensive research because of its potential application as solar cell (Motoyoshi et al. 2010; Ray 2001). This is due to its high solar absorbency, low thermal emittance, low cost materials and ease to fabricate (Maruyama 1998; Oral et al. 2004).

To date, many methods were used to grow CuO thin films. These include the reactive sputtering (Ogwu et al. 2005; Parretta et al. 1996; Pierson et al. 2003), chemical vapour deposition (CVD) (Maruyama 1998), sol-gel (Oral et al. 2004; Ray 2001) and thermal oxidation (Shanid & Khadar 2008).

Despite all the efforts, only few works reported on the deposition of CuO on different substrates (Ogale et al. 1992). For example, Ogale et al. (1992) studied the characteristics of CuO deposited by pulse excimer laser ablation on silicon (Si), magnesium oxide and zirconium dioxide substrates. Apart from that, it is still difficult to obtain a single phase CuO or pure CuO without mixtures of Cu, CuO and cuprous oxide (Cu_2O) phases. For example, Maruyama (1998) and Oral et al. (2004) obtained multi phases CuO crystalline thin films with atmospheric-pressure CVD and sol-gel-like methods, respectively. Meanwhile, by using reactive sputtering of a copper target with different conditions (i.e. ratio of oxygen and sputtering pressure), it has been shown that the tendencies to obtain multi phases crystalline and mixtures of Cu-O compounds and Cu (Ogwu et al. 2005; Parretta et al. 1996; Pierson et al. 2003).

In this work, we report on the growth and characterizations of the single phase CuO thin films on glass and Si substrates by the radio frequency (RF) sputtering method. Structural, optical and electrical properties of the deposited films were investigated by means of X-ray diffraction (XRD), atomic force microscopy (AFM), Fourier transform infrared (FTIR) spectrometer, ultra-violet visible (UV-Vis) spectrophotometer, four point probe techniques and Keithley 4200 semiconductor characterization system.

Experimental Details

Cupric oxide was deposited on glass (normal microscope slide) and n-type Si(100) substrates by using the A500 Edwards RF sputtering system at room temperature. The glass and Si substrate were rinsed with acetone and deionised water and dried with nitrogen gas. For the Si, it also dips onto dilute hydrofluoric acid to remove native oxide. Subsequently, the substrates were fixed on a rotating substrate holder at a distance of 10 cm above the target. The CuO target with a diameter of 76.2 mm and a purity of 99.95% was used. The base pressure of the chamber was better than 5.0×10^{-5} mbar.

During deposition, the RF power and pressure were maintained at 150 W and 2.0×10^{-2} mbar, respectively. Prior to deposition, the target was pre-sputtered for 5 min to remove any possible contamination. Then, CuO thin films were deposited for 60 min.

The crystalline structure of the films was examined by XRD (PANalytical X'Pert system) phase analysis (PA) method with CuK_α X-ray source. The films surface morphology was investigated by AFM (Dimension Edge from Bruker) with tapping mode. The scanning area was set at 2 × 2 μm. The composition of the films was examined by FTIR spectrometer (Spectrum GX FTIR, Perkin-Elmer). The measurement was carried out at an incident angle of 30° with the aid of a variable angle reflectance accessory in far infrared (FIR) region (300-700 cm^{-1}). The spectra are recorded using 128 scans at a resolution of 4 cm^{-1}. The optical band gap of the film was studied with UV-Vis (UV-1800 system from Shimadzu) transmission measurement in the range of 200-1100 nm. The thickness of the film was determined by the SEM cross-section method. The electrical properties of the film were measured using four point probe technique. Palladium (Pd) contact was deposited by RF sputtering on 1 mm diameter hole metal mask. Current-voltage (I-V) behaviour was obtained by Keithley 4200 semiconductor characterization system.

Results and Discussion

Structural Properties

Figure 1 shows the XRD PA pattern of the CuO thin films on glass and n-type Si(100) substrates. From the XRD patterns, the sample exhibits single diffraction peak at 35.43° for CuO thin film on glass substrate; while two diffraction peaks at 35.38° and 69.30° for CuO thin film on Si substrate. The strong peak at 69.30° is corresponding to the cubic Si(100). Based on the Joint Committee for Powder Diffraction Standards (JCPDS file No. 01-089-2531) data for CuO, the diffraction peak at around 35.4° is attributed to (-111) plane of monoclinic CuO. This indicated that the deposited CuO thin films consist of single phase monoclinic structure with preferred orientation (-111).

From Figure 1, it was found that the full width half maximum (FWHM) of the CuO(-111) diffraction peaks on glass and Si substrates were 0.25° and 0.22°. This indicated that the crystalline quality of CuO thin film on Si substrate is better as it has a smaller FWHM value. By using the Scherrer's equation, the crystallite size of the deposited films on glass and Si substrates were estimated to be 33.4 and 37.9 nm, respectively. Note that the Scherrer's equation is given by $D = K\lambda/B\cos\theta$, where K is the constant dependent on crystallite shape (0.9), λ is the X-ray wavelength (1.5406 Å), B is the FWHM and θ is the Bragg angle (Nakaoka et al. 2004).

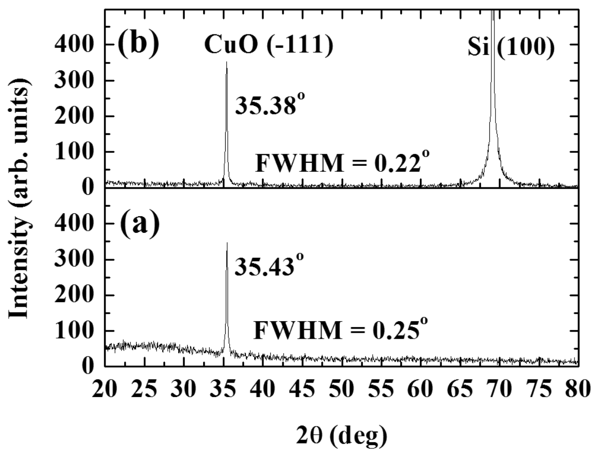

FIGURE 1. XRD phase analysis patterns of the CuO thin films on (a) glass and (b) Si(100) substrate

For CuO thin film on Si(100) substrate, the XRD peak has shifted to lower value, which is mostly due to the in-plane lattice mismatch between CuO and Si substrates. Note that the glass is amorphous and the top view of the atomic arrangement of cubic Si(100) is arrange in square (Dadgar et al. 2007). Meanwhile, the in-plane of the CuO(-111) is believed in triangle shape. Overall based on the XRD FWHM and peak intensity, CuO thin film on Si(100) substrate has slightly better crystalline quality as compared to glass substrate.

Figure 2 shows the three dimension (3-D) AFM images for the CuO thin films on glass and Si(100) substrates. As shown in Figure 2, the surface morphology of both samples showed well organized nano-pillar like structure. The root mean square (RMS) surface roughness of the CuO thin films were obtained by further analysed the AFM images using NanoScope Analysis software. The RMS surface roughness for CuO thin films on glass and Si(100) substrates were about 3.64 and 1.91 nm, respectively. The deposited CuO thin film on Si(100) substrate exhibits much smoother surface morphology as compared to the glass substrates.

OPTICAL PROPERTIES

Figure 3 shows the room temperature FIR reflectivity spectra of CuO thin films on glass and Si(100) substrates in the range of 300-700 cm^{-1}. Also shown in Figure 2(a) is the FIR reflectivity spectrum of glass substrate. Note that the Si is infrared inactive, therefore no peak is originated from Si substrate. For the glass substrate FIR spectrum, there is only one reflection peak which located at 465 cm^{-1}. This peak is corresponding to the transversal optical (TO) of glass mode, which is originated from Si-O-Si rocking vibration mode (Kirk 1988). The CuO thin film on glass substrate has one prominent reflection peak and a weak peak located at 437 and 535 cm^{-1}, respectively. The prominent peak is due to the TO mode of glass substrate (Kirk 1988). Meanwhile, CuO on Si substrate has one prominent reflection peak located at 525 cm^{-1}. The origin of the peak 525 and 535 cm^{-1} are the TO mode of the CuO (Lefez et al. 1995). Therefore, it is shown that the film has only CuO compound and is in good agreement with the XRD result.

Figure 4 shows the UV-Vis transmission spectrum of CuO thin film on glass substrate in the range of 200-

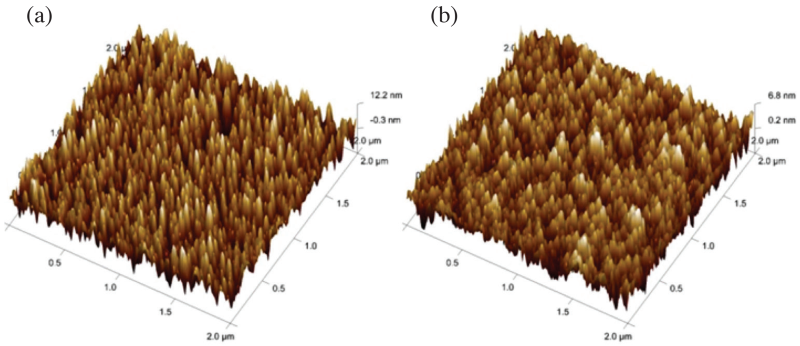

FIGURE 2. 3-D AFM images of the CuO thin films on (a) glass and (b) Si(100) substrates measured under a 2 × 2 μm scanning area

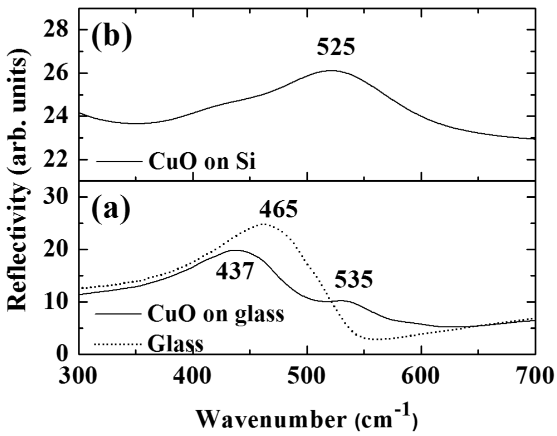

FIGURE 3. Room temperature far infrared reflectance spectra of CuO thin films on (a) glass and (b) Si(100) substrates in the range of 300-700 cm^{-1}

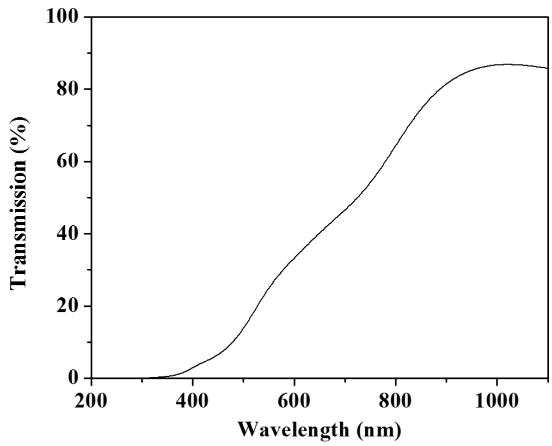

FIGURE 4. UV-Vis transmission spectrum of CuO thin film on the glass substrate in the range of 200-1100 nm

1100 nm. Note that the UV-Vis transmission spectrum for CuO thin film on Si(100) was not shown due to the zero transmission. As the wavelength of incident increases from 350 to 900 nm, it was found that the transmission of the film increases linearly. To determine the optical band gap, absorption coefficient (α) of the film was calculated using (1) (Ilican et al. 2007):

$$\alpha(\nu) = 2.303(Abs/t), \tag{1}$$

where *Abs* is the optical absorbance and *t* is the film thickness. The thickness of the CuO thin film was 190 nm as measured from the SEM cross-section image. The optical band gap of the films was estimated by means of Tauc's equation (Oral et al. 2004; Pierson et al. 2003):

$$\alpha h\nu = C(h\nu - E_g)^n, \tag{2}$$

where $h\nu$ is the energy of the incidence photon, C is a constant, E_g is the optical band gap, and value n is depending on quantum selection rules for the particular materials. Generally, n is 0.5 for materials possess direct band gap and n is 2 for indirect band gap (Shanid & Khadar 2008).

In this work, $n = 0.5$ was used because a straight line is obtained as we plotted the $(\alpha h\nu)^2$ versus $h\nu$. The graph $(\alpha h\nu)^2$ versus $h\nu$ for CuO thin film on glass substrate was shown in Figure 5. According to (2), the optical band gap was corresponding to the intercept of the straight line on the photon energy axis. Therefore, the sample possesses a direct band gap of 1.37 eV. Note that the obtained band gap was close to the band gap of the bulk CuO 1.3 eV (Serin et al. 2005) and in the range of the reported values. However, it was found that this value was smaller compared to the band gap of CuO deposited by means of reactive sputtering of Cu target method. For example, the band gap for the CuO thin films obtained by Pierson et al. (2003) and Ogwu et al. (2005) were 2.11 and 2.05 eV, respectively. The large difference of CuO band gaps was most possibly due to the crystalline quality of deposited CuO films. Obviously, the results showed that the band gap of the deposited CuO films is strongly dependence on the growth method.

ELECTRICAL PROPERTIES

From the four point probe measurements, resistance (*R*), sheet resistance (*Rs*) and resistively (ρ) of the CuO thin film on glass substrate were obtained. The *R*, *Rs* and ϱ is about 120 MΩ, 560 MΩ/sq, and 18 kΩ.cm, respectively. Note that the obtained values were the averaged of the five measurements. The resistively of the film obtained in this work was comparable to the Pierson et al. (2003) CuO thin films. From the electrical results, it shows that the sample is resistive.

Figure 6 shows the current-voltage (I-V) properties of the Pd contact on CuO thin films. It was shown that Pd exhibits ohmic and schottky contact for CuO thin films on glass and Si(100) substrates, respectively. Commonly, gold contact is used to form ohmic contact on CuO thin films due to it has a high work function. However, in this work Pd, which has similar work function as gold, can also form ohmic contact on CuO thin film on glass substrate. Therefore, Pd can also be considered as ohmic contact metal as it is cheaper than gold. The Schottky contact is obtained on CuO thin film on Si(100) substrate, mostly is due to the formation of CuO/Si pn junction and the depletion layer is extended into CuO thin film as it is resistive. Therefore, CuO thin film is depleted and affected the contact behaviour.

CONCLUSION

Single phase CuO thin film was successfully deposited on glass and Si(100) substrates using RF magnetron sputtering method. The XRD results showed that the CuO thin films have monoclinic structure with preferred CuO(-111) orientation. FIR reflectance results confirmed that the deposited films consisted of CuO without other mixtures. The film possesses a direct band gap with 1.37 eV. From the I-V behaviour, Pd exhibited ohmic and schottky

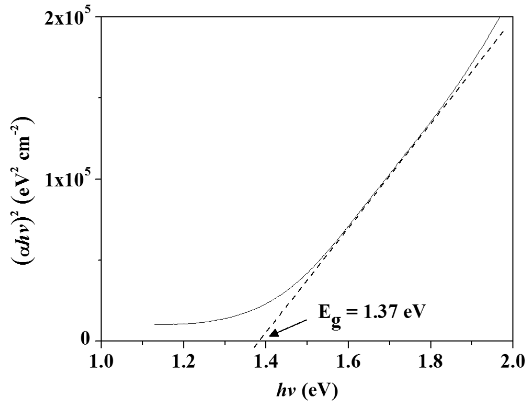

FIGURE 5. Graph $(\alpha h\nu)^2$ versus $h\nu$ for CuO thin film on glass substrate

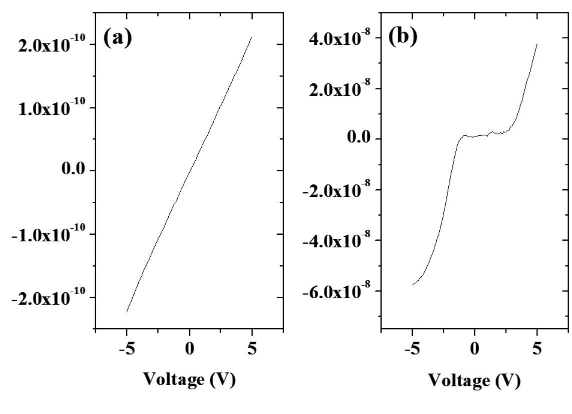

FIGURE 6. Current-voltage graphs of Pd contacts for CuO thin films on (a) glass and (b) Si(100) substrates

contacts for CuO thin films on glass and Si(100) substrates, respectively. However, the CuO film is resistive. Further work will be done to control the electrical properties of CuO thin films by performing the doping.

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