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Preparation and characterization of copper oxide thin films deposited by filtered cathodic vacuum arc

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Abstract

Copper oxide thin films deposited on Si (100) by a filtered cathodic vacuum arc with and without substrate bias have been studied by atomic force microscopy, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The results show that the substrate bias significantly affects the surface morphology, crystalline phases and texture. In the film deposited without bias, two phases—cupric oxide (CuO) and cuprous oxide (Cu$_2$O)—coexist as cross-evidenced by XRD, XPS and Raman analyses, whereas CuO is dominant concurrent with CuO (020) texture in the film deposited with bias. The film deposited with bias exhibits a more uniform and clearer surface morphology although both kinds of films are very smooth. Some explanations are given as well.

1. Introduction

Cupric oxide (CuO) and cuprous oxide (Cu$_2$O) are the two main semiconductor phases of copper oxide with narrow band-gap. It has been reported [1] that Cu$_2$O has a cubic crystal structure and a direct band-gap of 2.2 eV, while CuO has a monoclinic structure and an indirect band-gap of 1.4 eV. They have attracted much interest due to their potential applications in solar cells [2], magnetic devices [3] and catalysis [4, 5] and because they have radiation properties similar to those of an ideal black body. Another special fundamental characteristic of CuO and Cu$_2$O is the satellite structure on the high-energy side of valence and core levels in their x-ray photoelectron spectra (XPS) [6]. It is the satellites that provide important information on the electronic structure of these transition metal oxides. Rakhshani [2] documented a good review of the preparation, characterization and properties of copper oxide, where the techniques included high- and low-temperature oxidation, electro-deposition, anodic oxidation, chemical oxidation and reactive sputtering. Since then, many new techniques have been proposed to synthesize the copper oxide thin films and nanoparticles, such as activated reactive evaporation (ARE) [7], rapid liquid dehydration and precipitation [8], one-step solid state reaction [9] and the dip-coating technique [10].

Filtered cathodic vacuum arc (FCVA) deposition is a common method to prepare oxide, nitride and metal films, where various methods are employed to remove macroparticles inherent to arc evaporation itself. This arc source provides particles of high ionization rate and high ion energy (50–150 eV) for condensation on substrate. By using this technique, the resultant films can be obtained on a rather low substrate temperature. This is favourable for temperature-sensitive substrates such as plastic. Also thermal residual stress in the film could be low compared to other high temperature processes. On the other hand, the films usually adhere well due to the induced ion mixing by the bombardment of energetic particles. Recently, polycrystalline ZnO semiconductor thin films [11] and dense tetrahedral amorphous carbon films with high sp$^3$ [12] produced by FCVA have been reported. However, few studies have been conducted on the preparation and properties of copper oxide films by this technique.

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In this paper, we report on the preparation and characterization of copper oxide thin films synthesized by FCVA. The thin films were investigated by atomic force microscopy (AFM), x-ray diffraction (XRD), x-ray photoelectron spectrum (XPS) and Raman spectroscopy. The results show that the films could be pure cupric oxide or a mixture of cuprous and cupric oxides.

2. Experimental details

The FCVA system has been described elsewhere [13]. In brief, the system consists of three main components: a cathode target and anode pair, a filtering duct, and a sample chamber. The target arc is initiated by striking a graphite trigger to the target surface, and the plasma produced is sustained due to a DC voltage applied to the cathode–anode pair. The plasma is then steered out through the filtering duct into the sample chamber, where the ions impinge on the substrate and the thin films form. The filtering duct is applied not only to eliminate the unwanted macroparticles but also the neutral species from the plasma stream. A high purity Cu plate, 30 mm thick and 50 mm in diameter, was used as the cathode source. The deposition chamber, roughly pumped by a rotary pump, was evacuated to a base vacuum of $\sim 5 \times 10^{-6}$ Torr with a cryo-pump. Prior to deposition, the (100) n-type silicon wafer was in situ sputtered for 5 min by an Ar ion beam at $\sim 800$ eV and $\sim 200$ mA. During deposition, the arc current was set at 60 A. Simultaneously, a mixture of oxygen and argon gas, with 100 sccm and 5 sccm, respectively, was admitted into the cathode–anode region, where a small amount of Ar gas greatly improved the stability of the arc, possibly due to the fact that Ar plasma is easily ignited and sustained and reduces somewhat the oxidation of the target. Accordingly, the process pressure was $\sim 2 \times 10^{-4}$ Torr. Two types of samples were prepared: without bias (sample A) and with $-100$ V (sample B), respectively. The films deposited were both of the same thickness, around 120 nm.

The surface morphology and roughness of the thin films were characterized by atomic force microscope (AFM, Dimension 3000, Digital Instruments). The phase of the thin films was identified by XRD (x-ray diffractometer, D5005, SIEMENS) using Cu K$\alpha$ radiation (wavelength of 1.54 Å) at 40 kV and 40 mA with a thin film goniometer (Rigaku, Japan). The incident angle of the x-ray is 1˚. The chemical states of the atomic species in the thin films were analysed by XPS (Kratos AXIS spectrometer, UK) with the monochromatic Al K$\alpha$ x-ray radiation. The microstructure of the films was examined by Raman scattering using the 514.5 nm line of an Ar$^+$ laser as the excitation source.

3. Results and discussion

The AFM images for samples A and B are shown in figure 1. The surface of the copper oxide thin films obtained by FCVA is quite smooth, both of rms roughness less than 1 nm. This atomic-scale smoothness is a natural feature of the FCVA, i.e. high energy of depositing ions inducing high surface mobility. It is observed that sample B deposited with $-100$ V bias presents a more uniform and clearer morphology, as disclosed by XRD analyses, in which it is found that the film deposited with bias possesses smaller crystallites compared to the film deposited without bias. The clearer morphology is a result of the bias-enhanced sputtering, which removes some particles bonded with each other weakly, as reported in [14, 15].

Glancing angle XRD patterns of the two samples are shown in figure 2. As seen, both samples are of polycrystalline structures. For sample A, there are three strong XRD peaks at 2$\theta$ = 35˚, 36.6˚ and 42.2˚, corresponding to the (−111) and (002) crystal planes of CuO, (111) and (200) planes of Cu$_2$O, respectively. The weak peak at 2$\theta$ = 38.3˚ corresponds to the (111) and (200) planes of CuO crystal. Another wide and weak peak centred at 2$\theta$ = 55.4˚ is related to the contribution from the overlapping of the CuO (020) and (202) planes, as supported by the normal XRD analysis discussed below. This XRD pattern indicates that cupric and cuprous oxides coexist in sample A. In contrast, for sample B, besides the occurrence of the weak peak at 31.3˚, the peak at 35˚ greatly reduces in intensity whereas the peaks at 36.6˚ and 42.2˚ disappear.
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Figure 2. Glancing angle XRD patterns of samples A and B. It is seen that cupric and cuprous oxides coexist in sample A, whereas sample B is composed of the pure CuO phase.

The other two weak peaks at 38.3° and 55.4° hardly change in intensity. No obvious peak shift can be observed. It is interesting to note that all peaks are associated with CuO crystal planes for sample B, showing that the thin film deposited with bias voltage is a pure monoclinic CuO phase or that the fraction of crystalline Cu2O is so small that it cannot be detected. This indicates the substrate bias can noticeably affect the phase composition of copper oxide films. The great reduction in the peak at 35° is believed to be due to more defects existing in sample B, which are induced by bombardment of condensing ions with higher energy as compared with sample A. It is found that the crystallite size in sample B is reduced as evidenced by the peak widening and as reflected from the above AFM images. The grain refinement effect induced by strong ion-bombardment during deposition is often observed [16]. The average crystallite size can be calculated using the Scherrer equation [17]:

$$D = \frac{0.9\lambda}{B \cos \theta},$$

where \(\lambda\) is the x-ray wavelength, \(\theta\) is the Bragg diffraction angle, and \(B\) is the full-width at half-maximum (FWHM) of the peak corresponding to \(\theta\). When calculated by using the peak corresponding to the (002) plane of CuO, the resultant grain sizes are 9.3 nm and 5.4 nm, respectively, for samples A and B. Note that the FWHM of the peak is obtained by fitting the XRD patterns and using the Grams/32 software, which is a commercial software for a Renishaw Ramascope Spectrometer (RENISHAW, Gloucestershire, UK).

The textures of samples A and B are characterized by normal mode XRD spectra. As shown in figure 3, there are four strong peaks, corresponding to the CuO (−111) and (002), Cu2O (111), CuO (111) and (200), and Cu2O (200) planes, and the weak peak belonging to CuO (110) plane in sample A. However, for sample B, the peak corresponding to the CuO (020) plane is prominent while other peaks are greatly suppressed, denoting that CuO (020) preferential orientation occurs. From the normal mode XRD spectra, it is again observed that CuO and Cu2O coexist in sample A while CuO exists in sample B, consistent with the glancing angle XRD results.

Figure 3. Normal mode XRD patterns of samples A and B to characterize the texture of the samples. It is again observed that CuO and Cu2O coexist in sample A while CuO exists in sample B, consistent with the glancing angle XRD results.

Figure 4. Raman spectra of samples A and B, agreeing well with the XRD results for sample composition identification. The broadening of the Cu2O profile in sample B may be attributed to the amorphous characteristic of the phase which could not be detected by XRD.

Raman spectra of samples A and B are displayed in figure 4. For sample A, three peaks located at around 300, 340, 600 cm\(^{-1}\) are observed. Both the strong peak at 300 cm\(^{-1}\) and the weak peak at 340 cm\(^{-1}\) are ascribed to CuO [18]. The broad peak centred at 600 cm\(^{-1}\) is believed to be contributed by several Cu2O-related sub-peaks such as 570, 618 or 624 cm\(^{-1}\) [18, 19]. In contrast, for sample B, the CuO-related peaks at 300 and 340 cm\(^{-1}\) both become stronger. However, the broad peak at 600 cm\(^{-1}\) associated with Cu2O is largely suppressed in intensity. It is well-known that the intensity of Raman scattering is directly proportional to the number of scattering centres present in the volume illuminated by the laser beam. Thus, it is concluded that both CuO and Cu2O exist in sample A while CuO is dominant in sample B, agreeing with the result.
of XRD. We also note that the Cu$_2$O-related Raman peak does not disappear completely for sample B whereas the Cu$_2$O diffraction peak cannot be observed. This difference may exist because Cu$_2$O does not crystallize or the amount of crystalline Cu$_2$O is low so that it cannot be detected by XRD. Another possible explanation is that Raman scattering is more sensitive to copper oxide compared with XRD, as reported by Gong et al [18].

A possible reason for the different phases of copper oxide in the films with and without bias, could be that applying substrate bias during deposition induces impact-stimulated chemical composition variation in the resulting films. The application of bias may lead to more incorporation of oxygen into the films as in ion beam assisted deposition. In sample A without substrate bias, CuO and Cu$_2$O form simultaneously. However, by biasing the substrate, the extra-incorporated oxygen with higher energy is supposed to lead to the formation of CuO from Cu$_2$O, as indicated by the following reaction:

$$\text{Cu}_2\text{O} + \text{O} \rightarrow 2\text{CuO}.$$ 

As a consequence, the amount of Cu$_2$O in sample B is greatly reduced and almost undetectable by XRD as presented earlier. As a result, the crystalline phase changes with substrate bias correspondingly.

The survey spectra of XPS for both samples A and B are presented in figure 5. The spectra are globally similar to each other. The peaks corresponding to Cu 3d, 3p, 3s, 2p and Auger, O 1s and Auger are obviously observed. C 1s peak is also found, which is due to the exposure of the samples to air. No argon is seen, indicating that no argon exists in the samples or the argon content is lower than the detection limit. The high-resolution spectra corresponding to Cu 2p and O 1s are given in figures 6(a) and (b). They are plotted after correction of charging effects using a binding energy of 284.8 eV as the C 1s peak.

Figure 6(a) shows Cu 2p$_{3/2}$ and 2p$_{1/2}$ spectra. The respective main peaks of Cu 2p$_{3/2}$ for samples A and B lie at 933.7 and 933.8 eV. These main peaks can be assigned to Cu$^{2+}$ ions, rather than Cu$^{+}$ ions, which have a main peak at a lower binding energy of about 932.4 eV [20]. In addition to the main peaks of Cu 2p$_{3/2}$, their satellite peaks are also observed at higher binding energies. This satellite feature observed in both samples is an indication of materials having a partially filled d$^9$ shell configuration in the ground state, such as copper dihalides, metallic nickel, or CuO [20]. For Cu$_2$O with a completely filled shell (d$^{10}$), this satellite peak is absent because screening via a charge transfer into the d states is not allowed. Moreover, in both samples, the main peaks of 2p$_{3/2}$ are located at a binding energy that is 20 eV higher than that of their 2p$_{1/2}$ main peaks. The similarity of the Cu2p XPS spectra of samples A and B proves that these surfaces are both dominated by CuO. However, as concluded from the XRD analysis, Cu$_2$O exists in sample A. This difference is due to the fact that XPS, unlike XRD, can only get the composition information from surface rather than bulk. It is, therefore, concluded that CuO and Cu$_2$O coexist in sample A in which CuO is dominant on its surface, whereas only CuO is present in sample B. This assumption is supported by the Raman scattering analysis discussed earlier. Balamurugan et al [7] also reported that Cu$_2$O nanoparticles were capped with a surface layer of CuO, which stabilizes the more symmetric cuprous oxide phase.

There are two components (one main peak $S_1$ and one satellite $S_2$) in the O 1s spectra after curve decomposition is performed for both samples A and B, as shown in figure 6(b). The main peaks for both cases are located at 529.8 eV. The FWHM of the main peak of sample A is about 1.0 eV, which is slightly narrower than that of sample B (1.22 eV). Note that both the FWHM are larger than that of single crystal cupric oxide (0.8 eV), where the satellite component almost disappears [21]. The energy of the satellites in samples A and B are centred at approximately 1.6 eV and 2 eV higher than their main peaks, respectively. The area ratios of $S_1/S_2$ for samples A and B are about 1.41 and 0.65, respectively, meaning that sample B presents a larger satellite component. It is well-known that the main peak and satellites of O 1s spectra correspond to different chemical states of the oxygen atoms [22]. The main peak at lower binding energy is attributed to the normal O$^{2-}$, interacting with the copper atoms to form the chemical Cu–O bond. The satellite is ascribed to the extra-lattice oxygen [21], indicating non-stoichiometric nature of the thin films. This result fits well with the differential FWHM of the main peaks between our oxide thin films and the single crystal cupric oxide. Again, the more extra-lattice oxygen in sample B, i.e. a lower $S_1/S_2$ ratio, is attributed to the higher incorporated oxygen resulting from substrate bias.

It is worth mentioning that thermal annealing would change the composition/structure, and thus the properties, of the copper oxide thin film [23, 24]. Therefore, it is necessary and meaningful to further investigate how thermal annealing affects the structure and properties of the present copper oxide thin films.

### 4. Conclusions

Copper oxide thin films have been deposited on Si (100) by FCVA with and without substrate bias and investigated by AFM, XRD, x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The results show that substrate bias...
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Figure 6. (a) Cu 2p and (b) O 1s XPS spectra of samples A and B, showing that the surfaces are both dominated by CuO. Note that the CuO phase in sample A as detected by XRD is covered by the surface CuO layer, which was also reported by Balamurugan et al [7]. The difference between XPS and XRD is that XPS, unlike XRD, can only get the composition information from the surface rather than the bulk.

significantly affects the surface morphology, crystalline phases and texture. In the film deposited without bias, two phases—cupric oxide (CuO) and cuprous oxide (Cu2O)—coexist, whereas CuO is dominant concurrent with the CuO (020) texture in the film deposited with bias. Also, XRD suggests that the film prepared with bias has more defects compared to the film prepared without bias. Substrate bias makes the deposited film exhibit a more uniform and clearer surface morphology. By comparing samples A and B, it is found that the bias applied makes Cu2O convert to CuO due to more incorporation of oxygen, and also makes the film structure change partly from crystalline to amorphous, as evidenced by XRD.

References