Selective bias deposition of CuO thin film on unpolished Si wafer

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Abstract
In order to enhance the performances of CuO-based surface-sensitive materials and devices, one feasible scheme is depositing CuO thin films on textured Si wafers to enlarge the specific surface area. In this work, the bias deposition of CuO thin film on unpolished Si wafer was carried out in a RF balanced magnetron sputtering system. The as-achieved CuO thin film was further characterized with scanning electron microscope, powder x-ray diffractometer and ultraviolet-visible spectrophotometer. It was found that the CuO thin film shows a pyramid-textured film morphology consisting of composite structures: a loose and porous thinner film at the bottom of bevel, a dense and compact thicker film at the top of bevel and on the underside, and many nanosheets standing on the film surface. The tip charging effect and bevel influence were discussed to reveal the selective deposition mechanism of CuO thin film on the unpolished Si wafer. It was also demonstrated that the unpolished rough Si wafer surface seems more suitable for the crystallization of CuO along (002) orientation rather than (111) orientation. Meanwhile, the CuO thin film on unpolished Si wafer exhibits the strongest absorption at the wavelength of ~554 nm and a band gap of 1.94 eV, both of which show redshift relative to those of CuO thin film on polished Si wafer.

1. Introduction

Cupric oxide (CuO) is an important p-type transition metal oxide semiconductor material, which shows potential applications in the fields of solar cells [1, 2], electrodes [3, 4], catalysts [5, 6], gas sensors [7] and hydrogen detection [8]. In order to enhance the performances of these CuO-based surface-sensitive materials and devices, people can prepare CuO thin films of porous structure or deposit CuO thin films on textured Si wafers to obtain a higher specific surface area. In the existing literature, there have been many studies on the fabrication of porous CuO thin films [2–10] while few studies on the deposition of CuO thin films on textured Si wafers [2]. For the deposition of thin films on textured Si wafers, it can be roughly equivalent to a planar thin film deposition with an enlarged specific surface area in most cases. However, the film deposition will be seriously affected by the surface morphology or flatness of substrates in some special cases. For example, during glancing angle deposition [11, 12], the shadowing effect of rough substrate surface induces the columnar growth of thin films, which has been studied in detail. Recently, our group further demonstrated that when the glass slide substrate was positively or negatively biased, the tip charging effect of substrate surface would result in the formation of Cu2O porous nanostructured films [13, 14]. Nevertheless, we have not studied the bias deposition of CuO thin films on textured Si wafers under external electric field. It can be speculated that different substrate materials and surface morphology for the bias deposition of different deposits may have great differences in the deposition process and mechanism. Therefore, a detailed and in-depth study on the effect of surface morphology of textured Si wafers on the bias deposition of CuO thin films is very necessary.

With the above considerations, in this work we particularly studied the bias deposition of CuO thin films on unpolished Si wafers by magnetron sputtering. It was found that the as-prepared CuO thin film shows a diverse feature at different substrate locations such as the bevel and underside. Then the tip charging effect and bevel
influence were discussed to reveal the selective deposition mechanism of CuO thin film. Finally, the crystal structure and optical properties were also characterized and further compared with those of CuO thin film on polished Si wafer.

2. Experimental section

CuO thin films were deposited on unpolished and polished (for comparison) Si wafers respectively in a JGP500A mode radio-frequency (RF) balanced magnetron sputtering system at a substrate bias voltage of +50 V. A Cu target of 99.99 wt% purity and a steady flow of high pure Ar gas (15 sccm, 99.999 wt%) were applied for a physical sputtering. The chamber was evacuated to a base pressure of 2.0 \times 10^{-3} \text{ Pa. The sputtering deposition was carried out at a RF power of 80 W at room temperature and the deposition duration was controlled to be 60 min. The other details and parameters can be found in [13]. It has been demonstrated that the residual O}_2 in the pre-pumped vacuum chamber is the main oxygen source for the oxidation of sputtering Cu atoms [15]. Relative to the case in [13–15], the higher base pressure (2.0 \times 10^{-3} \text{ versus } 5.0 \times 10^{-4} \text{ Pa}) in this work can provide more sufficient O}_2 (2.08 \times 10^{11} \text{ versus } 5.2 \times 10^{10} \text{ atoms/cm}^2, \text{ four times}) for the oxidation of Cu atoms, which may result in the formation of CuO rather than Cu and Cu}_2O. The as-achieved CuO thin films were then characterized by a field-emission scanning electron microscope (SEM, ZEISS SUPRA 55), a powder x-ray diffractometer (XRD, RIGAKU D/MAX 2500 PC) and an ultraviolet-visible (UV–vis) spectrophotometer (METASH UV-9000S) to study their surface morphology, crystal structure and optical properties.

3. Results and discussion

Figures 1–2 show the top view and tilted view SEM images of CuO thin film deposited on unpolished Si wafer, respectively. As can be seen from figures 1(a), (b) and 2(a), the surface of the unpolished Si wafer is mainly composed of some intersecting bevels and undersides, which shows a typical pyramid-textured morphology. After deposition of CuO thin film, the surface morphology at different locations is greatly different. In detail, as shown in figures 1–2, the CuO thin film at the bottom of bevel is very thin, loose and shows porous structure, while the CuO thin film at the top of bevel and on the underside both seems thick, dense and compact. The

![Figure 1. Top view SEM images of different magnifications (a,b: 10,000×; c,d: 50,000×) showing the CuO thin film deposited on unpolished Si wafer. Figures 1(c), (d) are the enlarged images of locations ① (the bottom of bevel and the underside) and ② (the top of bevel) in figure 1(b), respectively.](image-url)
thickness of CuO thin film on the bevel decreases gradually from the top of bevel to the bottom of bevel, which
ranges from \( \sim 100 \) nm to \( \sim 30 \) nm. It was further observed that the bevel with a length of \( 1 \mu m \) or more seemed
easier to deposit CuO thin films selectively. In addition, the deposition angle on the bevel which was defined as
the angle between the normal of bevel surface and the incident flux was mostly around 60°. Here, such a
deposition angle was demonstrated to be suitable for the selective deposition. For comparison, figure 3 further

**Figure 2.** Tilted view SEM images of different magnifications (a: 10,000×; b: 50,000×) showing the CuO thin film deposited on unpolished Si wafer.

**Figure 3.** (a), (b) Top view SEM images of different magnifications (a): 10,000; (b): 50,000 and (c) cross sectional view SEM image showing the typical surface morphology of CuO thin film deposited on polished Si wafer.
shows the top view and cross sectional view SEM images of CuO thin film deposited on polished Si wafer. It can be observed that a uniform, flat and dense CuO thin film with a film thickness of ∼65 nm is obtained on the polished Si wafer surface. In addition, in contrast to the CuO thin film on polished Si wafer, there are also many CuO nanosheets standing on the surface of CuO thin film on unpolished Si wafer. The above different morphology of CuO thin films can only be attributed to the different Si wafer morphology since all the other deposition conditions are exactly the same. As illustrated in figure 4(a), the unpolished Si wafer can be decomposed into three typical different locations: ① tip; ② bevel; ③ underside.

1. At the tip of two intersecting bevels and nearby (i.e., at the top of bevel, see location ① in figure 4(a)), the tip charging effect will play an important role. When the Si wafer is positively biased, the resulting electrostatic charges will gather preferentially at the tip and nearby. As a result, the incident sputtering Cu atoms will be attracted by the tip charges and then preferentially deposit at the tip and nearby with a high deposition rate of ∼2.8 × 10^{-2} nm s^{-1}. Subsequently, the Cu atoms will be oxidized into CuO molecules and a thicker CuO film up to 100 nm in thickness is obtained therein.

2. On the bevel of unpolished Si wafer especially at its bottom (see location ② in figure 4(a)), there are two reasons leading to the thinning of films and even formation of a porous structure. One is most of the incident Cu atoms are attracted by and preferentially deposited at the adjacent tips, and the other one is the bevel increases the deposition area ($S \rightarrow S/\cos \theta = S_b$, see figure 4(a)). Both of these reasons lead to a low film deposition rate of ∼8.3 × 10^{-3} nm s^{-1} at the bottom of bevel. It is conservatively estimated from many titled view SEM images that the film thickness decreases by up to ∼70 nm from the top to the bottom of bevel, which confirms our above analysis. We also observed from SEM images that if the length of bevel was too short down to several hundreds of nanometer, it seemed difficult to deposit selectively. This may be because the location ② of the bevel cannot be distinguished clearly. In addition, for the formation of CuO nanosheets on the bevel, it may be attributed to the accumulation of stress in the film due to the directional diffusion of Cu atoms or CuO molecules downward along the bevel surface [16].

3. On the underside of unpolished Si wafer (see location ③ in figure 4(a)), it is smooth and flat on the surface. When bias voltage is applied to such a Si wafer location, there are little electrostatic charges on the underside. As a result, the incident Cu atoms are deposited to the underside without selectivity, resulting in formation of a uniform, flat and continuous CuO thin film with a medium deposition rate of 1.8 × 10^{-2} nm s^{-1}.

Figure 4. Schematic illustrations showing (a) selective deposition of CuO thin film at different locations (① tip, ② bevel and ③ plane) of unpolished Si wafer and (b) uniform deposition of CuO thin film on polished Si wafer.
While for the polished Si wafer with a smooth plane surface, as shown in figure 4(b), the resulting electrostatic charges under substrate bias voltage are uniformly distributed along the Si wafer surface. Consequently, the incident Cu atoms will be uniformly attracted by the uniform electrostatic field and finally a uniform, flat and compact CuO thin film is thus formed. Also note that the morphology of CuO thin film deposited on polished Si wafer is greatly different from that of Cu$_2$O thin film deposited on glass slide at a substrate bias of +50 V \[13\] although the substrate morphologies are both smooth and flat. This may be attributed to two possible reasons. One is the different mobilities of Cu atoms and CuO molecules on the surface of Si wafer with those of Cu atoms and Cu$_2$O molecules on the surface of glass slide, respectively. The other is the different distribution of electrostatic charges on the surface of a semiconductor Si wafer and an insulator glass slide.

Figure 5 further shows the XRD results of the CuO thin films deposited on polished and unpolished Si wafers. As observed from figure 5(a), the diffraction peaks at 2-Theta of 35.399 and 38.521 degree are well consistent with (002) and (111) orientations of CuO (JCPDS card no. 45-0937), respectively. No diffraction peaks of Cu and Cu$_2$O can be observed in the patterns, which demonstrates a pure CuO thin film by the full oxidation of sputtering Cu atoms. Moreover, no matter the CuO thin film is deposited on polished or unpolished Si wafer, as shown in figures 5(b), (c), the intensity and grain size of CuO (002) are respectively larger than those of CuO (111). This indicates that both CuO thin films exhibit a (002) preferred orientation to a
certain extent. In particular, when the CuO thin film is deposited on unpolished Si wafer, the intensity of CuO (111) decreases significantly although the grain size along (111) orientation increases a bit, which can be attributed to the decrease of CuO (111) grains in amount. Therefore, it may be concluded that the unpolished rough Si wafer surface seems more suitable for the crystallization of CuO along (002) orientation rather than (111) orientation. Alternatively, the change of relative intensity for the (111) and (002) peaks may also result from the change of diffraction geometry for the two types of thin films with different roughness.

The optical reflectance measurement of CuO thin films deposited on polished and unpolished Si wafers was carried out by a UV–vis spectrophotometer. As shown in figure 6, they exhibit the strongest absorption peaks at the wavelength of ~425 nm (violet light) and ~554 nm (green light), respectively. It indicates that when CuO thin film is deposited on unpolished Si wafer, a red shift of absorption peak occurs. Figure 7 further shows the \((F(R)hv)^2-hv\) curves and band gap of CuO thin films deposited on polished and unpolished Si wafers. Here, \(F(R) = (1 - R)^2/(2R)\) is the Kubelka-Munk diffuse reflectance formula and \(R\) is the reflectivity. By making the extension line of the linear part of \((F(R)hv)^2-hv\) curve, its intersection with the \(hv\) axis is the band gap value of

Figure 6. UV–vis reflectance curves of CuO thin films deposited on polished and unpolished Si wafers.

Figure 7. \((F(R)hv)^2-hv\) curves and band gap of CuO thin films deposited on polished and unpolished Si wafers.
CuO thin film. It can be found that the band gap of CuO thin films deposited on polished and unpolished Si wafers is estimated to be 2.03 and 1.94 eV respectively, which are both much larger than that of bulk CuO (1.2 eV). Since the band gap of a semiconductor film is affected by some factors such as quantum size or nanosize effect, doping and defect [15]. In the present case, the nanosize effect including effects of film thickness and building particle and sheet sizes, and the crystal defect in the film may both influence the band gap. In contrast to the CuO thin film on polished Si wafer, the CuO thin film on unpolished Si wafer with different film morphology and crystal structure may contribute to the deviation of band gap (2.03–1.94 = 0.09 eV).

4. Conclusions

In this work, the bias deposition of CuO thin film on unpolished Si wafer was investigated by RF balanced magnetron sputtering. It was found that the obtained CuO thin film shows a textured film morphology consisting of composite structures: a loose and porous thinner flm at the bottom of bevel, a dense and compact thicker film at the top of bevel and on the underside, and many nanosheets standing on the film surface. The tip charging effect and bevel influence were discussed to reveal the selective deposition mechanism of CuO thin film on the unpolished Si wafer. It was also demonstrated that the unpolished rough Si wafer surface seems more suitable for the crystallization of CuO along (002) orientation rather than (111) orientation. Meanwhile, the CuO thin film on unpolished Si wafer exhibits the strongest absorption at the wavelength of ~554 nm and a band gap of 1.94 eV, both of which show redshift relative to those of CuO thin film on polished Si wafer. It is expected that such a textured CuO composite structure film has the advantages of large specific surface area, multi-structure composite, and thus may meet the performance requirements of function, structure and stability in practical application.

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