Cu$_2$O porous nanostructured films fabricated by positive bias sputtering deposition

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Abstract
In this work, the authors fabricated Cu$_2$O porous nanostructured films (PNFs) on glass slide substrates by the newly developed positive bias deposition approach in a balanced magnetron sputtering (MS) system. It was found that the surface morphology, crystal structure and optical property of the as-deposited products were greatly dependent on the applied positive substrate bias. In particular, when the substrate was biased at +50 and +150 V, both of the as-prepared Cu$_2$O PNFs exhibited a unique triangular pyramid-like structure with obvious edges and corners and little gluing, a preferred orientation of (111) and a blue shift of energy band gap at 2.35 eV. Quantitative calculation results indicated that the traditional bombardment effects of electrons and sputtering argon ions were both negligible during the bias deposition in the balanced MS system. Instead, a new model of tip charging effect was further proposed to account for the controllable formation of PNFs by the balanced bias sputtering deposition.

Keywords: Cu$_2$O, porous nanostructured films, balanced magnetron sputtering, positive bias deposition

(Some figures may appear in colour only in the online journal)

1. Introduction

As one of the most common two kinds of copper oxides, cuprous oxide (Cu$_2$O) is an important p-type transition metal oxide semiconductor material. Due to the advantages of low-cost, non-toxicity and abundant copper sources and the potential applications in the fields of gas sensors [1, 2], solar cells [3, 4] and photocatalysts [5–7], Cu$_2$O thin films have attracted great interest of researchers. In order to enhance the performances of the above Cu$_2$O-based surface-sensitive devices and materials, the researchers tend to prepare Cu$_2$O thin films of porous or nanoporous structures [2, 6, 8]. In literature, people often concentrates on the porosity and surface area of porous or nanoporous films while the unique size or curvature effect [9, 10] of nanoscale building units or nanostructures has not attracted sufficient attention. Based on this consideration, a special kind of porous thin films which consists of solid and/or hollow nanostructures, such as nanoparticles, nanoligaments, nanowires, nanoplates, nanocavities, nanopores or nanochannels, is proposed herein. We call such porous nanostructure-films or nanostructured films hereafter porous nanostructured films (PNFs) for short. Due to the unique size or curvature effect of building nanostructures along with the increased porosity and surface area, it is

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expected that such thin films of PNF structures may have some different or improved performances in contrast to the traditional porous and solid thin films [11, 12]. Thus, it makes great sense to fabricate Cu2O PNFs with tunable building nanostructures and further study their corresponding properties.

In the existing literature, the main preparation methods of Cu2O films include direct oxidation [13–15], electrochemical deposition [16–18] and magnetron sputtering (MS) [19–22]. However, these methods have not been found for the preparation of Cu2O porous films, especially the Cu2O PNFs with excellent properties of nanoscale building units. Instead, people prefer to utilize the templating [23], sol–gel [24] and dealloying [25] methods to prepare porous films. However, all of these conventional methods for the preparation of porous films have disadvantages more or less. For example, the pore shape and size distribution of porous films prepared by templating is determined by the template and thus seem not flexible or less-diversity. The porous films prepared by sol–gel method have the faults of high shrinkage rate, poor adhesion, easy cracking and residual hydroxyl and carbon in the film. Dealloying was initially proposed for the fabrication of porous metal thick films and then was further developed to fabricate metal oxide PNFs by Su et al [11, 12]. Nevertheless, both of them may introduce impurities to the porous films from the solution. Therefore, it is very imperative to find or develop a new approach for the preparation of PNFs to overcome the above shortcomings. As we all known, MS is a commonly used method to prepare high quality thin films at present. It will not introduce other impurities and has the advantages of simple equipment, easy control, large coating area and strong adhesion. In fact, porous metal thin films such as Ti [26] and porous semiconductor (composite) thin films such as Zn/ZnO [27] and TiO2 [28] have been successfully prepared by direct-current MS method. Similarly, can we also use MS equipment or make some targeted improvement to realize the flexible preparation of Cu2O PNFs?

With the above considerations, in this work we successfully prepared various Cu2O PNFs by our newly developed positive bias sputtering deposition approach via adjusting the applied substrate bias voltage in a balanced MS system. It was observed that the surface morphology, crystal structure (or texture) and optical property of the as-prepared Cu2O PNFs were greatly dependent on the applied substrate bias voltage. A new mechanism of tip charging effect was proposed for a full explanation of the substrate bias voltage-dependent formation of PNFs while the traditional ion bombardment effect was demonstrated to be negligible.

2. Experimental section

All samples were deposited onto glass slides in a JGP500A mode radio-frequency balanced MS system. A Cu target of 99.99 wt% purity was fixed to a 6 kGs magnetic cathode, which was connected with a 13.56 MHz RF power supply. The distance between the Cu target and the glass slide substrate was set to be ~15 cm. The chamber was evacuated to a base pressure of 5.0 × 10⁻¹⁰ Pa and subsequently back-filled with a steady flow of high pure Ar (15 sccm, 99.999 wt%) to maintain a chamber pressure of 0.10 Pa. Note that no external oxygen gas flow was introduced to the chamber due to the sufficient residual oxygen in the pre-pumped high vacuum chamber [29]. Before each deposition, a pre-sputtering deposition was carried out at a radio-frequency power of 80 W, which led to a deposition rate of ~0.045 nm s⁻¹. During the deposition, the substrate mounted on a 3 inch Cu substrate holder was biased using a direct-current power supply at 0 V, +50 V, +100 V, +150 V and +200 V, respectively. The film thicknesses were monitored by a quartz crystal oscillator and subsequently back-filled with Ar. Note that no external bias voltage was introduced to the chamber due to the sufficient residual oxygen in the high vacuum chamber [29]. The as-achieved deposits were characterized by field-emission scanning electron microscope (FESEM, ZEISS SUPRA 55), powder x-ray diffractometer (XRD, RIGAKU D/Max 2500 PC) and ultraviolet–visible (UV–vis) spectrophotometer (SHIMADZU UV-2450).

3. Results and discussion

3.1. Surface morphology

FESEM images in figure 1 show the typical surface morphology of the Cu2O films prepared under different substrate bias voltage. It can be seen from the micrographs that all the Cu2O films have the characteristics of large area, well-distributed, smooth surface and PNF structure. However, the details of their building nanostructures are quite different. When no external bias voltage is applied (Vb = 0 V), as shown in figure 1(a), the film presents a bicontinuous ‘ligament-channel’ PNF structure. Most of the ligaments are curved ropes shape, short in length, glued to each other and only partly with obvious edges and corners. The average diameters of the ligaments and channels are ~27 nm and ~15 nm respectively. When the substrate is biased at +50 V, as shown in figure 1(b), nanoscale triangular pyramids with cut sharp edges and corners appear on the PNF surface and little gluing can be seen between each other. The average side length of the pyramids is ~48 nm and the average pore diameter is ~13 nm. When the substrate bias voltage is further increased to +100 and +150 V, as shown in figures 1(c) and (d), both of the obtained films exhibit a triangular pyramids-like PNF structure more or less. The pyramids in figure 1(c) seem to glue to each other (like the case in figure 1(a)) while the pyramids in figure 1(d) show obvious edges and corners (like the case in figure 1(b)). Furthermore, the pyramids and pores in figures 1(c) and (d) are larger than those respectively in figure 1(b). For the average side length of pyramids: 71 nm in figure 1(c) and 69 nm in figure 1(d) versus 48 nm in figure 1(b); for the average pore diameter: 21 nm in figure 1(c) and 20 nm in figure 1(d) versus 13 nm in figure 1(b). When the substrate bias voltage further rises up to +200 V, as shown in figure 1(e), the film displays a typical ‘particle-void’ porous structure with
average diameters of particles and voids around 62 nm and 19 nm respectively. Based on the above observation, it can thus be concluded that the influence of substrate bias on the surface morphology is not linear. It implies that there may be two or more factors acting together or competing with each other.

3.2. Crystal structure

The grazing-incidence XRD (GIXRD) patterns in figure 2(a) show the crystal structure of Cu$_2$O PNFs under different substrate bias voltage. Comparing with the standard card, it is found that the diffraction peaks in the patterns coincide well with those of Cu$_2$O (card number: JCPDS-34-1354), and no other impurity peaks such as Cu and CuO are found in the patterns. It indicates that all the samples are pure Cu$_2$O films, and the bias voltage does not change the chemical composition of the products. It can be further seen from the patterns that all the Cu$_2$O films show a strong (111) preferred orientation, while the intensity of the diffraction peaks in other crystal orientations such as (110), (200), (220) and (311) are very weak and thus can almost be ignored. Since the out of plane GIXRD method was used in the experiment, it measured the crystal plane parallel to the surface of the film sample. This indicates that the orientation of Cu$_2$O grains is almost the same in the growth direction of the films (perpendicular to the film surface), all of which are (111) direction. In particular, we further study the relationships of the diffraction peak intensity and the grain size of Cu$_2$O (111) with the positive bias voltage of the substrate, as shown in figure 2(b). It is found that, with the increase of substrate bias voltage, the diffraction peak intensity of Cu$_2$O (111) decreases first and then increases, and reaches the minimum value at $V_s = +50$ V. On the contrary, the calculation result by Scherrer Formula shows that the grain size of Cu$_2$O (111) increases first and then decreases with the increase of substrate bias voltage, and reaches the maximum value at $V_s = +50$ V. This complementary relationship may be because the number of grains in the film is inversely proportional to the size of grains. It is thus concluded that the influences of substrate bias on the diffraction peak intensity and the grain size are both not linear. Similar to the case of surface morphology, it further indicates that there may be two or more factors acting together or competing with each other.

3.3. Optical property

Figure 3 gives the $(Ahv)^2 \sim hv$ curves of the Cu$_2$O PNFs prepared under different substrate bias voltage, where $A$ is the
that when the substrate bias is $V_s = 0$, +100 and +200 V, the values of the forbidden bandwidth are all 2.0 eV, while when the substrate bias is $V_s = +50$ V and +150 V, the forbidden bandwidth values are 2.2 eV and 2.35 eV respectively. It demonstrates that Cu$_2$O PNFs with different bandwidth can be prepared by adjusting the substrate bias voltage. Further, the above bandwidth values deviate from that of Cu$_2$O bulk material (2.17 eV): red shift at $V_s = 0$, +100 and +200 V; blue shift at $V_s = +50$ and +150 V. It is expected that the surface morphology and the crystallinity may both affect the bandwidth of PNFs. This is because the bandwidth of PNFs is not only related to the band structure of materials, but also affected by some other factors such as quantum size or nanosize effect, doping and defects [29]. In this work, firstly for different morphology with different distribution of surface nanocurvature, the nanosize effect (especially the nanocurvature effect [9, 10]) of the building nanostructures such as ligaments, pyramids and particles in PNFs will be accordingly different; secondly for different crystallinity, the effect of defects and grain size in the building nanostructures on the bandwidth of PNFs may be also different. Based on the above morphological and structural findings, it can be found that the morphology and the crystallinity both influence the bandwidth of Cu$_2$O PNF but in a nonlinear way. Further, we infer that the unique triangular pyramid structure of Cu$_2$O PNFs with obvious edges and corners and less gluing (see figures 1(b) and (d)) may contribute more to the blue shift of energy band gap. On the contrary, the other PNF structures without obvious edges and corners or with more gluing (see figures 1(a), (c) and (e)) may mainly lead to the red shift of energy band gap. At this level, the above optical experiment results are understandable although the specific influence mechanism is still unclear.

3.4. Bias deposition mechanism

Through the above analysis, we find that the surface morphology, crystal structure and optical property of the Cu$_2$O PNF change accordingly when different positive bias voltage is applied on the substrate. This means that a certain effect of substrate bias plays an important role during the bias deposition of Cu$_2$O PNF. In the existing literature, the research on bias deposition is mainly focused on the thin films prepared under a negative substrate bias in an unbalanced MS system [30–32]. One of the most notable feature of the unbalanced MS system is that part of its magnetic field lines can extend to the location of the substrate. Under the electric field of negative substrate bias, the positive sputtering ions such as Ar$^+$ can fly energetically to the substrate and then bombard the growing film effectively. As a result, a dense and solid film without porous structure is often obtained [30–32]. By contrast, almost all the magnetic field lines in the balanced MS system are bound near the target and thus only a very few sputtering ions or electrons can fly to the far substrate and bombard the growing film. As illustrated in figure 4(a), when a bias voltage $V_s$ is applied on the substrate, some of the sputtering ions (such as Ar$^+$, for negative bias voltage case) or electrons (e$^-$, for positive bias voltage case) may pass...
through the magnetic field of the target and reach the substrate. We measured the electric current \( I \) (mA) in the circuit at different positive and negative bias voltage \( V_s \) (V), which is shown in figure 4(b). Meanwhile, the electric current \( I \) can be expressed using the following equation according to its definition:

\[
I = nqvS,
\]

where \( n, v \) are the concentration and velocity of \( \text{Ar}^+ \) or \( e^- \) respectively near the substrate, \( q = 1.6 \times 10^{-19} \) C, and \( S \) is the basal area of the 3 inch Cu substrate holder.

As driven by the electric field of negative or positive substrate bias, some of the \( \text{Ar}^+ \) or \( e^- \) would be accelerated respectively and travel through the working gas in the chamber. Meanwhile, the \( \text{Ar}^+ \) or \( e^- \) would collide with the gas atoms and degrade the energy on their way to the substrate. According to equation (8) in [33], the average retained energy \( E_{k1} \) of \( \text{Ar}^+ \) or \( e^- \) before reaching the substrate can be similarly expressed by the following equation:

\[
E_{k1} = \frac{1}{2}mv^2 = (qV_s + E_{k0}) \exp (-\alpha d/\lambda),
\]

where \( \alpha \) is a constant (\( \alpha = 0.835 \) for the case of Cu target and Ar sputtering gas [33]), \( d = 15 \) cm, represents the distance between the target and the substrate, \( \lambda \) is the mean free path of \( \text{Ar}^+ \) or \( e^- \) (8.06 cm for \( \text{Ar}^+ \) and 9.32 \( \times \) \( 10^9 \) m for \( e^- \) under an Ar pressure of 0.10 Pa [34]), and \( E_{k0} \) is the initial kinetic energy of \( \text{Ar}^+ \) or \( e^- \) when escaping from the plasma region. As opposed to tens or even hundreds of the substrate bias, here the initial kinetic energy \( E_{k0} \) is negligible for simplicity. Thus, the simplified expression of the average retained energy \( E_{k1} \) can be given as in the following:

\[
E_{k1} = \frac{1}{2}mv^2 = qV_s \exp (-\alpha d/\lambda).
\]

According to equation (3), the average retained energy \( E_{k1} \) of \( \text{Ar}^+ \) (\( E_{k1,\text{Ar}^+} \)) or \( e^- \) (\( E_{k1,\text{e}^-} \)) under different substrate bias is shown in table 1. Combining equations (1) and (3), we can further get the expression of the concentration of \( \text{Ar}^+ \) or \( e^- \) close to the substrate:

\[
n = \frac{m}{2qV_s \exp (-\alpha d/\lambda)} \frac{I}{qS}.
\]

According to equation (4), we can calculate the concentration values of \( \text{Ar}^+ \) (\( n_{\text{Ar}^+} \)) and \( e^- \) (\( n_{\text{e}^-} \)) close to the substrate at different substrate bias, which are shown in table 1. It can be found that the order of magnitude of the concentrations are \( 10^{13} \) and \( 10^{15} \) m\(^\text{3}\) for \( e^- \) and \( \text{Ar}^+ \) respectively. On the other hand, the concentration of Ar atoms in the working environment is \( 2.5 \times 10^{18} \) m\(^\text{3}\) in plasma. Obviously, either a positive bias or a negative bias, even as high as 200 V, the concentration of \( e^- \) or \( \text{Ar}^+ \) close to the substrate is far less than that in plasma. It indicates that in the balanced MS system only a very small percentage of \( e^- \) or \( \text{Ar}^+ \) (\( \sim 0.001\% \) for \( e^- \) and \( \sim 0.1\% \) for \( \text{Ar}^+ \)) can escape from the localized magnetic field of the target and finally reach the substrate. Furthermore, the concentration of Cu atoms (will be further oxidized into Cu\(_2\)O subsequently) or Cu\(_2\)O molecules in the growing Cu\(_2\)O film is estimated to be \( \sim 10^{22} \) m\(^\text{3}\), which is much larger than that of the incident \( e^- \) (10\(^{15}\)) and \( \text{Ar}^+ \) (10\(^{13}\)). In this calculation, we assumed that the density of the growing Cu/Cu\(_2\)O film is the same as that of bulk Cu and Cu\(_2\)O respectively for simplicity. It demonstrates that only a very small portion of Cu atoms or Cu\(_2\)O molecules in the growing film of Cu\(_2\)O is bombarded by the \( e^- \) or \( \text{Ar}^+ \) on the biased substrate.

When the incident \( e^- \) or \( \text{Ar}^+ \) bombards the Cu atoms or Cu\(_2\)O molecules on the substrate, the transfer of energy will be carried out. In this process, we assume that both energy and momentum are conserved for simplicity. Therefore, the transferred energy (\( E_{k2} \)) to the Cu atoms or Cu\(_2\)O molecules
can be expressed by the following equation:

\[ E_{k2} = \frac{4m_1m_2}{(m_1 + m_2)^2} E_{k1}, \]  

(5)

where \( m_1 \) is the mass of an Ar\(^+\) or an e\(^-\), and \( m_2 \) is the mass of a Cu atom or a Cu\(_2\)O molecule. After a simple calculation, we can obtain the transferred energy to the Cu atoms \( (E_{k2,Cu}) \) or Cu\(_2\)O molecules \( (E_{k2,Cu2O}) \), as listed in table 1. When the positive substrate bias is applied, it is found that only a little energy in the range of \((0.08-0.69) \times 10^3 \) eV is transferred to the Cu atom or Cu\(_2\)O molecule. Also considering the low concentration of incident e\(^-\), it can thus be concluded that the little bombardment of e\(^-\) will make not big enough and significant change to the deposited film. In contrast, when the negative substrate bias is applied, the energy in the range of 7.2–40 eV is transferred to the Cu atom or Cu\(_2\)O molecule. It is expected that such a big energy transfer would cause the (self)-diffusion or even re-sputtering of the deposited Cu atoms or Cu\(_2\)O molecules on the substrate. Nevertheless, due to the low concentration of incident Ar\(^+\), it is also expected that a poor bombardment of Ar\(^+\) will work during the film deposition. In contrast to the negative substrate bias, however, it is obviously a better choice to apply the positive substrate bias for the formation of PNFs due to the less bombardment effect and the resulting less opportunity to form dense films.

In the above, we have excluded the impact of bombardment of Ar\(^+\) and e\(^-\) on the bias deposition of thin films, especially the bombardment of e\(^-\) during the positive bias deposition, in the balanced MS system. In the following, we propose a new model instead for the present positive bias deposition of Cu\(_2\)O PNFs. As schematically illustrated in figure 5(a), since the film surface is uneven with tips or particles at the nanoscale, according to the tip charging effect, the charges induced by Coulomb force will gather preferentially at the tips or on the surface of particles. Thus, the electric field near the film surface can be regarded as a superposition of electric fields of the massive point charges. Under the electric field of point charges, the material atoms or molecules which fly to the substrate will be subject to the forces from two aspects. On one hand, the atoms or molecules of the material is polarized so that the centers of positive charge and negative charge appear to be separated (see figure 5(a)). Since the electric field of point charge is inhomogeneous (increases as the distance decreases), the polarized Cu atoms or Cu\(_2\)O molecules will be attracted by the nearest point charges especially when they get close to the substrate (Force I). On the other hand, because of the repulsion between the same kind of charges, the atoms or molecules deposited at the tips and charged with the same charges will be excluded and bound by the electric field of the surrounding homologous charges (Force II). For the former, the point charge field provides an additional kinetic energy to the incoming atoms or molecules, which will promote the subsequent diffusion and migration on the surface of the substrate. For the later, the binding of the electric fields of the surrounding point charges will hinder the diffusion and migration of the material atoms or molecules between
different tips or on the substrate surface. It must be pointed out that the tip charging effect exists in the entire deposition process as long as the positive bias voltage is applied. As a consequence, it universally induces a columnar growth of the film along the normal direction of the substrate (as evidenced by the FESEM image in figure 5(b), take the substrate bias of +50 V for example) and a significant Cu$_2$O (111)-preferred orientation (see figure 2(a)) under the drive of reducing the system energy. However, the contradictory effects of Force I and II will exist in each bias deposition process of thin films. The different contribution of these two effects at different substrate bias voltage will influence or even determine the final morphology and structure of the films. (1) When $V_s$ = 0 V, there is no effect of substrate bias. The as-deposited Cu atoms or Cu$_2$O molecules have no sufficient energy to ensure the effective diffusion and migration on the substrate, and also can not selectively deposit at the tip of the film surface. As a result, the surface of Cu$_2$O film presents a randomly-oriented bicontinuous ‘ligament-channel’ PNF structure. (2) When $V_s$ = +50 V and +150 V, Force II plays the major role. Under the constraint of the electric field of one’s own locating tip, the Cu atoms or Cu$_2$O molecules deposit and grow in a columnar form. Meanwhile, the adsorption of Cu atoms or Cu$_2$O molecules is also affected by the neighboring tip fields, which likely leads to a lateral face-selective adsorption, thereby causing an anisotropic crystal growth of triangular pyramids with little adhesion to each other. (3) When $V_s$ = +100 V and +200 V, the contribution of Force I is greater than that of Force II. The atoms or molecules deposited at the tips will further diffuse along the surface of the film to a certain extent, so that the surface of the film is more glued and compacted. The above deduction on the contribution of Force I and Force II is mainly based on the combination of the SEM observation and the analysis of the tip charging effect. In fact, the Force I and Force II would both increase with the applied substrate bias voltage. However, the Force I and Force II are also greatly influenced by the tips shape and distribution on the growing film surface, which are adjusting in real time. As a result, at current stage it is very complicated to achieve a quantitative analysis on the contribution ratios of Force I and Force II at different bias voltages.

In the balanced MS, we believe that the deposition mechanism for negative substrate bias is similar to that for positive substrate bias. However, there are still some differences, big or small, besides the above-mentioned bombardment effect of e$^-$ and Ar$^+$. As we know, the mobility of electrons and holes in a semiconductor film is different. Consequently, they differ on the response speed under the positive and negative bias and the feedback effect of the tip charging. In general, the mobility of electrons is higher than that of holes. Thus, we infer that the response speed of electrons is faster than that of holes, and it is easier to gather electrons at the tips of the film, and thus the negative bias effect will be more obvious. Similarly, the carriers in the metal film are electrons, and the electrons can be more easily aggregated on the tips under the negative bias. In contrast, the metal cations are much more passive at the tips of the film surface under the positive bias. Based on this, we think that the effects of positive and negative bias on the tip charging effect or the bias deposition effect of the film will be different although a quantitative analysis is missing.

4. Conclusions

In this work, we successfully fabricated Cu$_2$O PNFs on positively-biased substrates in a balanced MS system. It was found that the morphology, structure and optical property of the as-deposited products were non-linearly dependent on the applied positive substrate bias. In particular, when the substrate was biased at +50 and +150 V, both of the obtained Cu$_2$O PNFs exhibited a triangular pyramids-like structure with obvious edges and corners and little gluing, a preferred orientation of (111) and a blue shift of energy band gap at 2.35 eV. Quantitative calculation results indicated that the traditional bombardment effects of electrons and sputtering ions were both negligible during the bias deposition in the balanced MS system. Based on the experiment results and the related theoretical analysis, a new model of tip charging effect was further proposed to account for the flexible formation of PNFs by the balanced bias sputtering deposition.

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