Temperature dependence of Cu_2O orientations in the oxidation of Cu (111)/ZnO (0001) by oxygen plasma*

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The role of temperature on the oxidation dynamics of Cu_2O on ZnO (0001) was investigated during the oxidation of Cu (111)/ZnO (0001) by using oxygen plasma as the oxidant. A transition from single crystalline Cu_2O (111) orientation to micro-zone phase separation with multiple orientations was revealed when the oxidation temperature increased above 300 °C. The experimental results clearly show the effect of the oxidation temperature with the assistance of oxygen plasma on changing the morphology of Cu (111) film and enhancing the lateral nucleation and migration abilities of cuprous oxides. A vertical top-down oxidation mode and a lateral migration model were proposed to explain the different nucleation and growth dynamics of the temperature-dependent oxidation process in the oxidation of Cu (111)/ZnO (0001).

Keywords: Cu_2O, oxidation, plasma, molecular beam epitaxy

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1. Introduction

Cuprous oxide (Cu_2O) has been considered a promising material for photovoltaic device applications due to its direct band gap of ~ 2.1 eV and its high absorption coefficient, which allows for a high solar energy conversion efficiency. The theoretical conversion efficiency of a Cu_2O-based solar cell is predicted to be up to 20%, which is very appealing because of several significant advantages, such as nontoxicity, abundant reserves, and low cost.[1,2] As intrinsically a p-type semiconductor, the heterostructure of p-Cu_2O with n-ZnO is of special interest because of the natural formation of a hetero p–n junction suitable for solar cell applications.[3−14] However, the best efficiency ever reported is just 3.83%[14] owing to the inferior crystal and interface qualities of the heterostructure. Such devices strongly depend on the stacking of very high-quality thin films with minimal surface roughness and controllable crystallinity.

As a commonly used synthesis method, the oxidation of Cu (Cu single crystals in most cases) has been extensively investigated, most of which focused on the studies of the surface oxidation process by using some conventional ultrahigh vacuum (UHV) research tools.[15−19] Recently, Luo *et al.* proposed a kinetic model to clarify their observation of the influence of oxygen pressure (from $\sim 7\times10^{-3}$ Pa to $\sim 2\times10^{4}$ Pa) as a driving force for the transition of Cu_2O nucleation orientation.[20] As the first step to form a Cu_2O film with good crystallinity on a single crystal ZnO (0001) surface, Ozawa *et al.* studied the atomic and electronic structures of the Cu_2O/ZnO (0001) interface obtained by the oxidation of Cu overlayer with a thickness up to 6.5 monolayer.[18] In that work, the oxidation conditions were fixed at 650 K with O_2 atmosphere of 1.3×10^{-4} Pa. It can be seen that the role of oxidation temperature on the Cu_2O orientation and crystallinity was not significantly considered, especially in the case of Cu/ZnO (0001) with a thicker

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Cu film which is essential for device applications. Additionally, oxygen gas instead of active oxygen radicals was commonly employed as the oxidant. Therefore, to bridge the gap between theory and experiments, research on the temperature-dependent oxidation dynamics of Cu/ZnO (0001) using the oxygen plasma is undoubtedly necessary for preparing high-quality Cu_2O/ZnO (0001) heterostructures.

Herein, we present our important findings of the dependence of Cu_2O orientations on the oxidation temperature and the corresponding dynamic process in the approach to establish a single crystalline Cu_2O film on ZnO (0001). These observations are of significance both for the understanding of metal/semiconductor oxidation physics and for the achievement of high quality heterojunction devices. We focus on the system of Cu_2O on ZnO (0001) because it is more promising to achieve a high solar energy conversion efficiency as well as the availability of high-quality single crystalline ZnO template. Oxygen plasma instead of oxygen gas is adopted as the oxidation source, which implies a much higher oxidation ability and different nucleation processes and growth dynamics.[21,22] An oxygen pressure of $\sim 10^{-3}$ Pa is applied due to the requirements of thicker films for device fabrication than those for surface science studies. The previous reports demonstrated that oxidizing Cu (111) would result in a Cu_2O (111) surface.[15–19] Interestingly, we can obtain (110) and (100) components besides (111) under the oxidation condition of high temperature and the oxygen plasma environment, which is attributed to the lateral expansion of Cu_2O (110) and Cu_2O (100) on the exposed ZnO (0001) surface via the assistance of oxygen radicals.

2. Experiments

The samples were fabricated by the oxidation of a Cu (111) layer on ZnO (0001) in a radio-frequency plasma assisted molecular beam epitaxy (rf-MBE) system. Elemental Zn (7N) and Cu (6N) evaporated by Knudsen cells and oxygen radicals (5N5) generated by the rf-plasma system were used as atomic sources for the growth. Single crystal ZnO (0001) layers each with a thickness around 300 nm were firstly prepared on *c*-plane sapphire wafers as the templates for Cu_2O growth.[23] It should be noted that the polarity of the ZnO films was delicately controlled by varying the thickness of the MgO buffer,[24] and its influence on the oxidation process was accordingly investigated, but no difference was found between Zn and O polarities. An intrinsic ZnO film with a resistivity higher than 6000 Ω·cm was necessary due to the requirement of electrical measurements of the upper Cu_2O layer. The reflection of high-energy electron diffraction (RHEED) patterns and the atomic force microscope (AFM) images showed that the ZnO films had smooth surfaces and were high quality, providing good templates for the following epitaxial growth. Cu_2O films were then synthesized in two steps. Firstly, a single crystal Cu (111) film with a thickness of 50–150 nm was deposited on the intrinsic ZnO template under a UHV background ($\sim 10^{-7}$ Pa). Secondly, the Cu (111) film was exposed to the oxygen plasma with a pressure in a range from 1.0×10^{-3} Pa to 5.0×10^{-3} Pa, an rf power of 150–250 W, and a substrate temperature varying from 300 °C to 750 °C. We monitored the whole oxidation progress mainly using the *in-situ* RHEED technique. The rf power and the oxygen gas flux were accordingly tuned to ensure a similar oxidation rate at different temperatures. A complete oxidation with no Cu left and no CuO formation was guaranteed by a delicate control of the oxidation parameters. A detailed investigation of the crystal structures and the temperature effects was conducted with X-ray diffraction (XRD) experiments in the National Synchrotron Radiation Lab, Hefei. A systematic characterization of the samples' surface morphology was performed in the AFM (Seiko) facility to assist the understanding of the oxidation dynamics.

3. Results and discussion

The whole growth process was *in-situ* recorded using RHEED. Figures 1(a) and 1(b) show the RHEED patterns of the Zn-polar ZnO template and the Cu film, respectively. ZnO (0001) and Cu (111) have similar in-plane atomic arrangements, but the mismatch is as big as 21.3%. When we deposit Cu at low temperatures, that is, below 300 °C, we will obtain a film with a smooth surface reflected by the streaky RHEED patterns (Fig. 1(b)). The AFM image displays some hexagonal holes in between the terraces (not shown here). This smooth Cu film will be changed to have an incontinuous morphology (Cu islands) at higher temperatures, as shown by the dim spotty RHEED patterns and the AFM images, which is induced by the relatively large interface energy of the metal/semiconductor system. Note that the Cu films of both morphologies are both (111) oriented

confirmed by XRD. All the Cu films in the present studies were fabricated at 300 °C, which enables us to understand the role of oxidation temperature on the evolution of Cu_2O orientations.

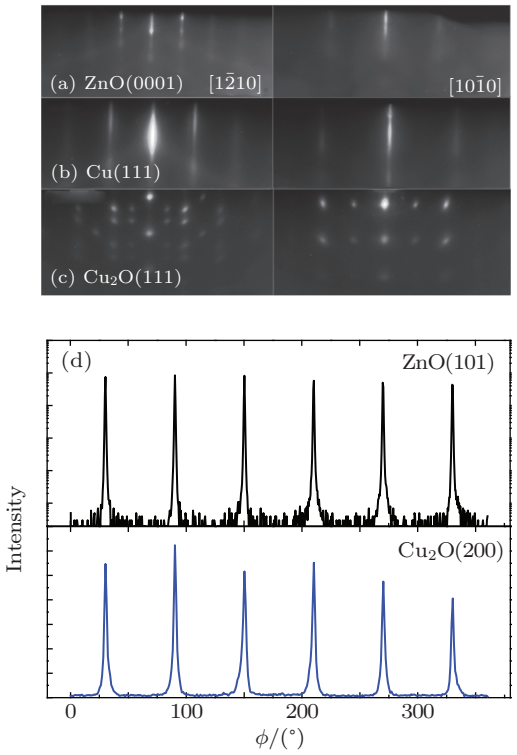


Fig. 1. (colour online) RHEED patterns with incident electron beams along [1$\bar{2}$10] and [10$\bar{1}$0] ZnO azimuths, respectively, obtained (a) from ZnO(0001) surface, (b) after Cu (111) deposition, (c) after oxidation of Cu (111) film at 300 °C. Panel (d) shows the XRD ϕ scan results of Cu_2O (200) and ZnO (10$\bar{1}$1).

The oxidation of the as-grown Cu (111) film on ZnO (0001) was firstly performed at 300 °C, considering the limited oxidation depth at lower temperatures. It can be clearly seen that a (111) orientated single crystalline Cu_2O film is obtained with 180° twin crystals, which is quite common for cubic-structured crystals (Fig. 1(c)). The crystallinity of Cu_2O (111) is further confirmed by the observation of six peaks with the same angle intervals in the ϕ scan of ZnO (10$\bar{1}$1) and Cu_2O (200) (Fig. 1(d)). Combining the ϕ scan results with the corresponding RHEED patterns, we confirm that a single crystalline Cu_2O (111) film is realized by the oxidation of Cu (111) on ZnO (0001) at low temperatures ($\leq$ 300 °C), and the in-plane epitaxial relationship between the two semiconductors can be easily concluded to be Cu_2O [11$\bar{2}$]//ZnO [10$\bar{1}$0] and Cu_2O [1$\bar{1}$0]//ZnO [1$\bar{2}$10]. The mismatch between ZnO (0001) and Cu_2O (111) is calculated to be 7.1% using the bulk lattice constants.

As mentioned above, the oxygen plasma possesses a much higher oxidation ability (including a higher oxidation speed and larger oxidation depth) than the oxygen gas. At low pressure ($\sim 10^{-3}$ Pa), the oxidizing ability of the oxygen gas is very weak. Even hours of exposure of the Cu film in a 10^{-3} Pa oxygen gas environment at 300 °C only forms a very thin oxide layer, which can be reduced to Cu through vacuum annealing for a few minutes. This process has been clearly observed by using the *in-situ* RHEED. The results are similar in the cases of higher oxidation temperatures. However, using oxygen radicals instead of the gas as the oxidant will definitely change the nucleation and growth dynamics of the oxidation process, which will be verified in the following experiments. As solid evidence, we can obtain a pure CuO film at a high temperature (such as 600 °C) and 10^{-3} Pa, which is impossible using the gas source according to the phase diagram.[25] Lyubinetsky *et al.* have studied the growth of Cu_2O (100) nanoclusters on $SrTiO_3$ (100) by using oxygen plasma, and they also found that the phase diagram as a function of oxygen pressure and growth temperature is quite different from the bulk. The growth window for Cu_2O was narrow, and the phase boundary was not sharp with some multiphase-coexistent regions, which they attributed to the small size effect.[26] However, the much stronger oxidizing ability of the oxygen plasma may be neglected. In our work, we observe the important role of the oxygen plasma in the Cu–Cu_2O–CuO phase transitions, which is reflected by the precise tuning of oxidation temperature, oxygen pressure as well as rf power, and oxidation time. By fixing the first two parameters and increasing the last one, the 100 nm thick Cu film will undergo a phase transition from Cu to Cu/Cu_2O, then pure Cu_2O, Cu_2O/CuO, and finally pure CuO.

The sensitivity of Cu oxide stoichiometry to the oxidizing parameters in the oxygen-plasma assisted growth would surely introduce difficulties to the efforts of the fabrication of single phase Cu_2O. However, in our experiments, the formation of CuO can be readily detected with the convenient *in-situ* RHEED monitoring, because the RHEED patterns of Cu_2O and CuO are distinguishable, and serve as a fingerprint of the complete oxidation of the Cu film into a single phase Cu_2O. XPS scans of core level Cu $2p_{3/2}$ were carried out on these samples to confirm the crystal phases. It shows clearly that at the surface, the Cu $2p_{3/2}$ signal can be simulated as a summation of two peaks located at 932.2 eV and 933.5 eV respectively by us-

ing the Gaussian fit (not shown here), while that of the as-sputtered surface (the top 5 nm layer was sputtered off) only consists of the former component. The 932.2 eV peak comes from Cu^{+}, and 933.5 eV corresponds to Cu^{2+}. The XPS results indicate that there is little CuO on the top surfaces of our samples, which can be easily understood. The very thin CuO cover layer might enhance the stability of Cu_2O as suggested by Balamurugan *et al.*[27]

Due to the existence of a Cu vacancy, the intrinsic Cu_2O is conclusively p-type conductive, which has been supported by many theoretical and experimental research results.[28,29] However, some groups claim that they obtained n-type Cu_2O (especially those grown by the electrodeposition method), and some explanations were put forward.[30,31] In our case, the clean MBE system would not introduce impurities to the film, which will affect the precise electrical measurements. Moreover, we choose the optimized growth parameters to get a high resistive ZnO film, which eliminates the influence from the ZnO layer underneath, and we control the oxidizing progress to avoid the existence of residual metallic Cu. Hall measurements give definite p-type data with a mobility of 40–80 cm/Vs, a resistivity of 100–400 Ω·cm, and a hole concentration of 10^{14}–10^{15} cm^{-3}. Furthermore, considering that the persistent photoconductivity of Cu_2O might reduce the precision of the results, we also check the conduction type by tracing the Hall voltage in varied magnet fields besides the conventional Van der Pauw measurement. The details of this method have been reported in our previous work.[32] All the completely oxidized Cu_2O samples show a p-type conductivity without exception. It should be noted that only the incompletely oxidized samples and those grown on low resistant ZnO templates would show n-type conductivity. So we suggest that the abnormal n-type conductivities of undoped Cu_2O reported before may come from the n-type substrates or the remaining metallic Cu.

We have demonstrated that the oxidation of Cu (111) film on a ZnO (0001) template by the oxygen plasma can produce a single crystalline p-Cu_2O (111) film at 300 °C, the subsequent experiments were carried out to illustrate the temperature-dependent oxidation dynamics of different Cu_2O orientations. Figure 2 shows the XRD θ–2θ scan curves of the Cu_2O films on the ZnO (0001) template fabricated at different temperatures. No peak from metallic Cu or over-oxidized CuO is observed throughout the temperature range in our experiments, indicating a precise control of the oxidation process. Unlike the oxidation achievement of single crystalline Cu_2O (111) at 300 °C, Cu_2O (110) and (100) orientations also Appear, forming a multi-orientated Cu_2O as the temperature increases. Meanwhile, as the oxidizing temperature increases from 300 °C to 750 °C, the full width at half maximum (FWHM) of the rocking curves of Cu_2O (111) decreases from 2.7° to 0.5° (not shown here). The emergence of Cu_2O (110) and (100) is interesting, as it is not in accordance with previous reports that suggest the Cu (111) film would only be oxidized to Cu_2O (111).[15–19]

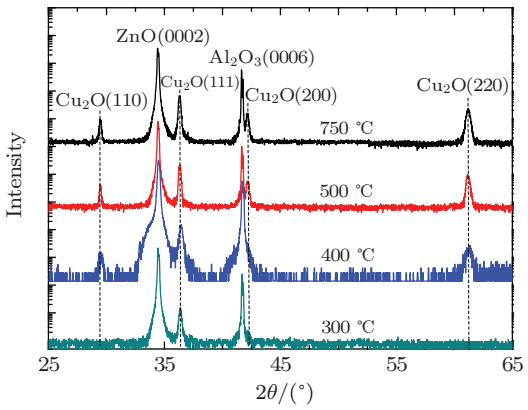


Fig. 2. (colour online) XRD θ–2θ scan of Cu_2O films oxidized at different temperatures.

In order to explore the mechanism of the temperature-dependent Cu_2O orientation transitions, we investigated the surface morphologies of these samples. Figures 3(a) and 3(b) show the AFM images of the Cu_2O samples oxidized at 300 °C and 750 °C, respectively. It can be seen that the morphologies of these two films are quite different. The low-temperature oxidized Cu_2O (111) sample has a relatively uniform surface, while the sample oxidized at the higher temperature presents a rough surface feature with hills and plains. A high-resolution image of the plain region displays the existence of rectangular islands (Fig. 3(c)), while that of the hill region shows an irregular hexagonal structure with terraces (Fig. 3(d)). The micro morphology is indicative of the crystal structure. Combined with the XRD characterization, we propose that a micro-zone phase separation occurs in this surface. That is, the hills have hexagonal atomic arrangements and are (111) oriented Cu_2O. The plains have a cubic structure and are (110) or (100) oriented. It is quite convincing to attribute the Cu_2O (111) portion to the top-down oxidation of Cu (111). The formation processes of (110) and (100) orientations, however, should be different from that of the (111) component.

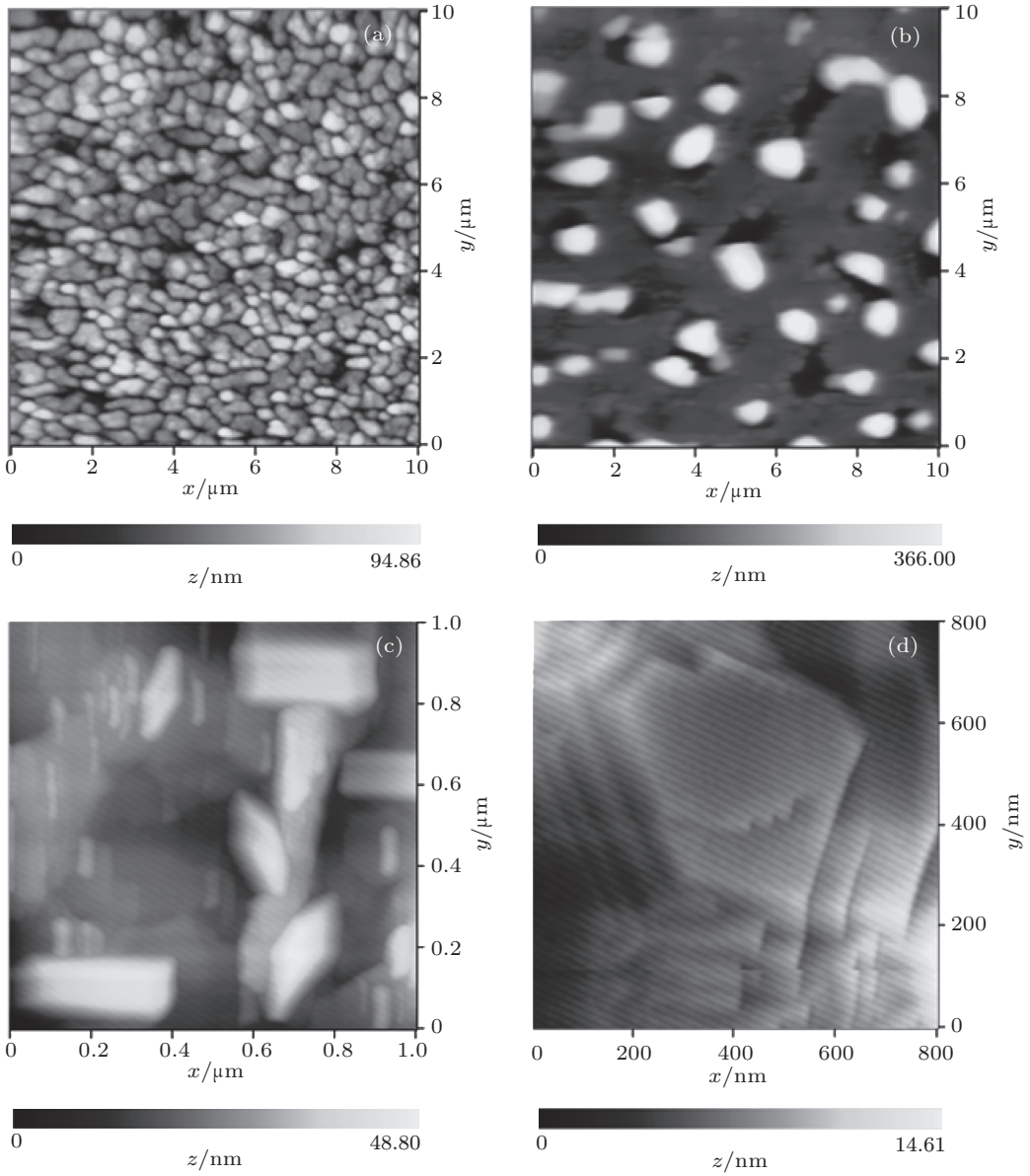


Fig. 3. AFM images of the Cu_2O films oxidized at (a) 300 °C and (b) 750 °C, as well as ((c) and (d)) the high-resolution micro-zone details of the 750 °C-oxidized sample.

We have observed an interesting phenomenon during the vacuum annealing process that the original continuous Cu film can be congregated into big islands leaving parts of the ZnO layer uncovered. We speculate that the exposed ZnO lattice will provide suitable nucleation centers for Cu_2O (110) or Cu_2O (100), which can migrate laterally from different steps of Cu (111) islands at higher temperatures with the great assistance of oxygen radicals. Jeong and Aydil have synthesized Cu_2O (110) on ZnO (0001) by using the metalorganic chemical vapor deposition,[9] suggesting that Cu_2O would preferentially grow on ZnO (0001) along the (110) orientation. The Cu_2O (111) face has the same hexagonal atomic arrangement as ZnO (0001), but for Cu_2O (110) or (100) on ZnO (0001), the epitaxial relationship is somewhat complex, because it actually requires a rectangular or square atomic cell grown on a hexagonal one. However, in the domain match mode (periodic coincidence match mode), Cu_2O (110) growing on ZnO (0001) is possible. The in-plane mismatches are about 1.5% and 7.3% along the two directions of the rectangular cell, respectively. Combined with the non-polar plane fact, it implies a smaller lattice mismatch and strain as well as a lower interface and surface energy compared to the case of Cu_2O (111) on ZnO (0001).[9] However, it simultaneously indicates the insurmountable obstacle to fabricate high-quality single crystalline Cu_2O (110)

on ZnO (0001) due to the rotation domains. Cu_2O (100) has a similar story with the lattice mismatches of 1.5% and 1.1%.

To support our viewpoint on this unique oxidation dynamic, we designed another experiment as below. Firstly, we carry out vacuum annealing of a smooth Cu (111) film at 750 °C to get a Cu island film with the ZnO layer exposed, which is testified to be still (111) oriented. Then we oxidized this Cu (111) film at 300 °C. According to our assumption, the (110) and the (100) orientated components will be suppressed compared to the sample oxidized at higher temperatures, because the temperature is too low to provide enough energy for the lateral migration of Cu_2O (110) or Cu_2O (100). The XRD measurements do prove that only (111) orientated Cu_2O is achieved (not shown here). The evolution of surface morphology is further investigated by AFM images of the continuous Cu film before the vacuum anneal, the as-annealed Cu islands, and the oxidized film, as shown in Fig. 4. It is quite clear that the continuous Cu film forms islands along with the appearance of part of the ZnO surface in this vacuum anneal process. Moreover, the exposed ZnO remains uncovered after the low temperature oxidation, which excludes the possibility of the lateral migration of Cu_2O (110) or Cu_2O (100). The main difference of the surface morphologies between Cu and Cu_2O islands is the change of height, which becomes larger after the oxidation because of the oxygen incorporation. Both the horizontal shape and the size are kept nearly the same, which is in agreement with our assumption. When oxidized at a low temperature, the oxidation occurs at the top surface and Cu_2O grows down to the lower layer so that only Cu_2O (111) is able to form. That is how we can obtain a single crystalline Cu_2O (111) film.

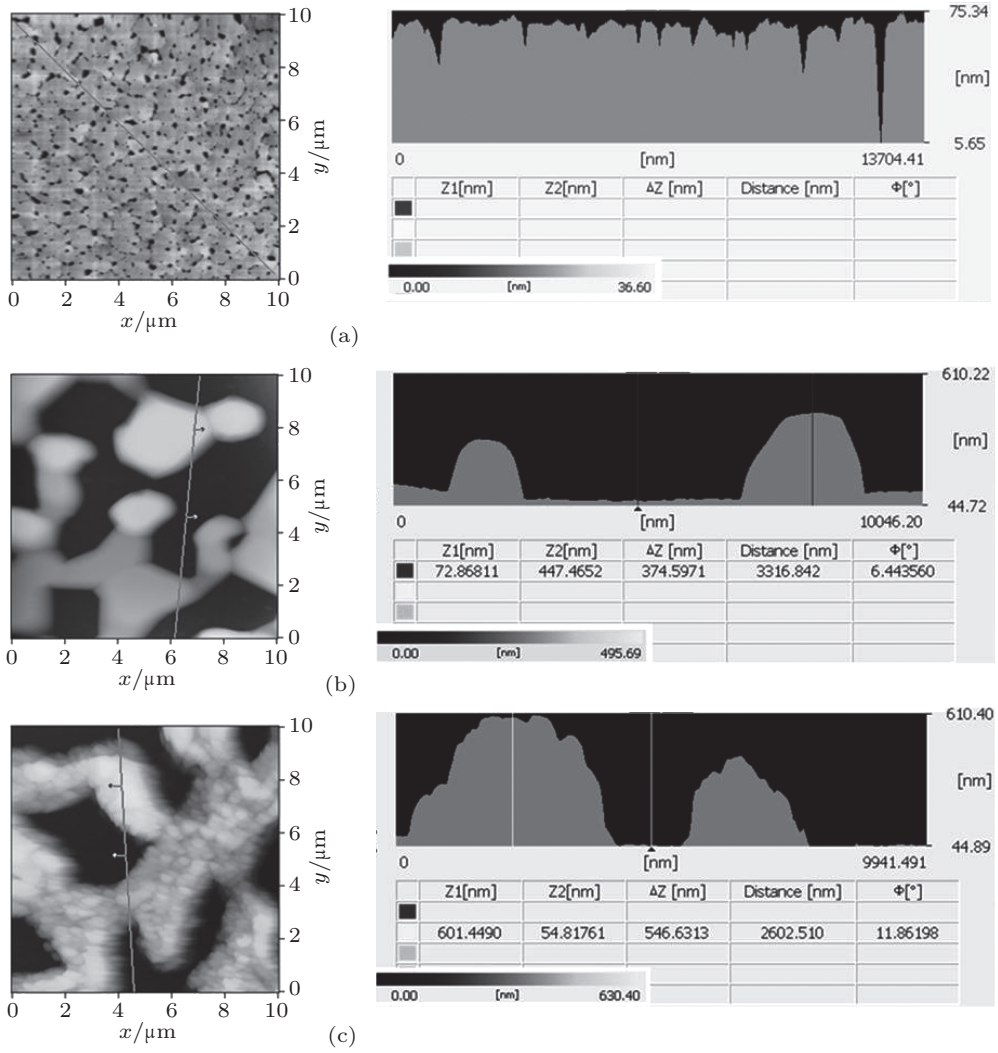


Fig. 4. AFM images tracing the fabrication process of the Cu_2O (111) film oxidized at 300 °C using 750 °C-annealed Cu (111) film. Panels (a), (b), and (c) show the continuous Cu film before the vacuum anneal, the as-annealed Cu islands, and the oxidized film, respectively.

If the oxidation is performed at a higher temperature, the Cu atoms around the steps of the Cu (111) islands will overcome the energy barrier and migrate laterally onto the uncovered ZnO surface lattice with the help of oxygen radicals, and the formation of Cu_2O (110) or Cu_2O (100) will therefore be enhanced. The following experiments were carried out at 650 °C with different oxidation times (all of them were not completely oxidized) to confirm the above-mentioned oxidizing process. XRD θ–2θ scans in Fig. 5(a) present that when the oxidation time increases, the intensities of Cu_2O related peaks increase, while the Cu (111) peak decreases. The corresponding AFM images show that Cu_2O (110) and (100) have covered the exposed ZnO (0001) surface in the first 10 min and change little when the oxidation time increases (Fig. 5(b)), which implies that the expansion of these components is so quick at high temperatures that a very thin (110) and (100) Cu_2O film has covered almost the whole exposed ZnO surface initially and then grows thicker and thicker as the oxidation carries on.

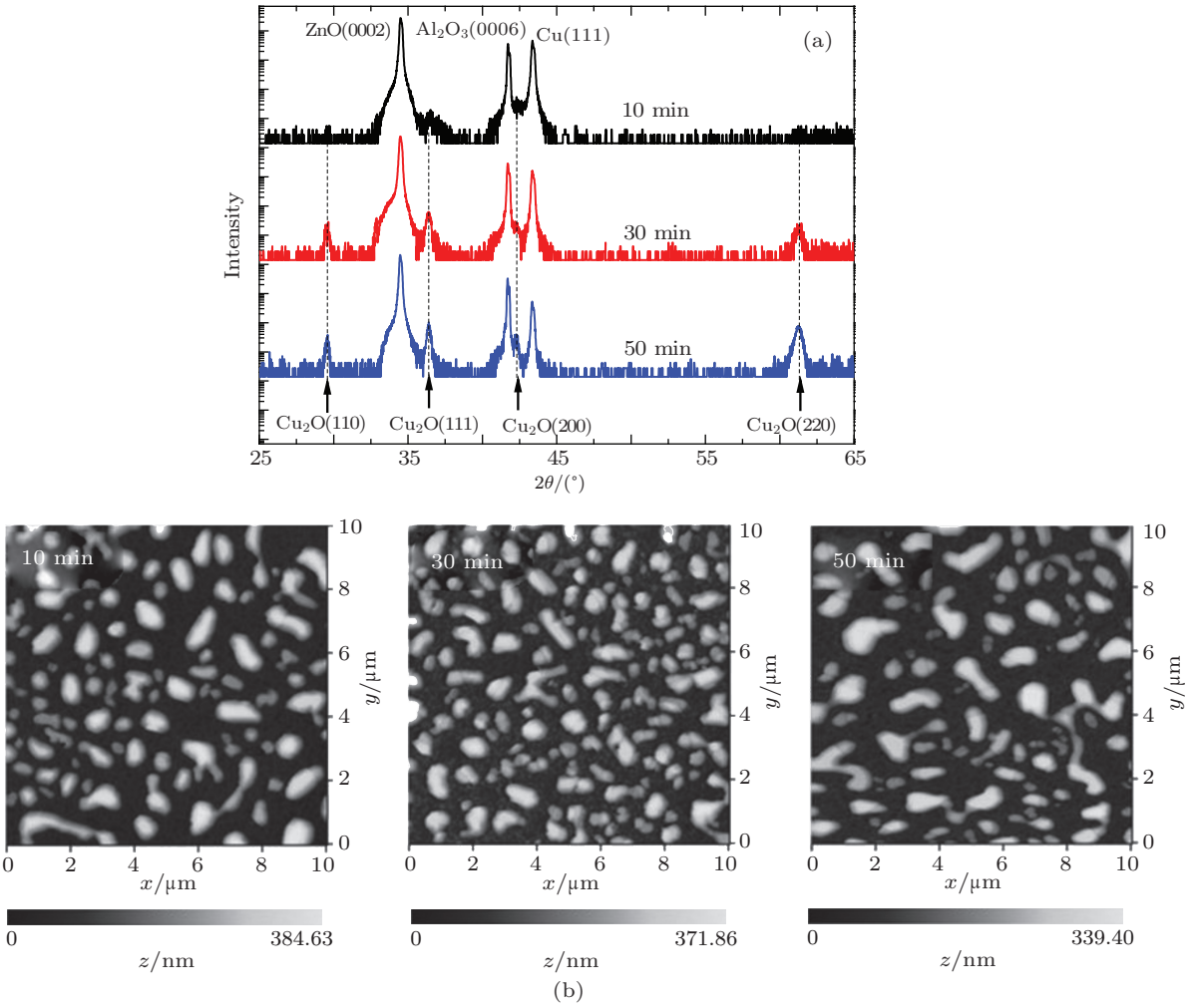


Fig. 5. (colour online) (a) XRD θ–2θ scans and (b) AFM images of Cu_2O films oxidized at 650 °C with different oxidation times.

With the evidence above, the temperature-dependent oxidation dynamics and the orientation selection behavior of Cu (111)/ZnO (0001) can be described by a schematic illustration shown in Fig. 6. A continuous Cu (111) film will form on the smooth ZnO (0001) surface at a low temperature, and its morphology displays a strong temperature dependence, which mostly decides the following oxidation behavior and results. At low temperatures, say 300 °C, the Cu_2O (111) orientation will be naturally realized through the vertical migration of Cu atoms which are then oxidized at the top of the film (vertical growth), in accordance with the previous oxidation studies of Cu (111). As the oxidation temperature rises up, Cu_2O (110) and

(100) besides Cu_2O (111) will be formed by the lateral migration of oxidized Cu atoms on the ZnO surface as follows. Firstly, Cu atoms at the edges of Cu islands will overcome the energy barrier to migrate onto the ZnO surface and be oxidized by the oxygen plasma, then these initial copper oxides nucleate on the exposed ZnO surface, quickly expand and cover all the exposed areas, and grow thicker and thicker (lateral growth).

Based on the knowledge we obtained from the oxidation process of Cu (111) on ZnO (111), it can be easily deduced that the epitaxial growth of Cu_2O on ZnO by using the oxygen plasma will yield (110) or (100) oriented film. Our synthesis efforts of Cu_2O using MBE prove that on a ZnO (0001) template, Cu_2O (110) is definitely favorable in accordance with Ref. [9]. However, some kind of 60° rotation domains would inevitably exist in this Cu_2O (110) film, which is undesirable for the promotion of film qualities and device performance. Our achievements of single crystalline Cu_2O (111) in this oxidation research make it possible to greatly improve the crystal quality of Cu_2O epitaxial film on ZnO (0001), and more details will be reported elsewhere. In addition, a previous report claimed the preference of (111) oriented Cu_2O on the hexagonal GaN (0001) surface.[33]

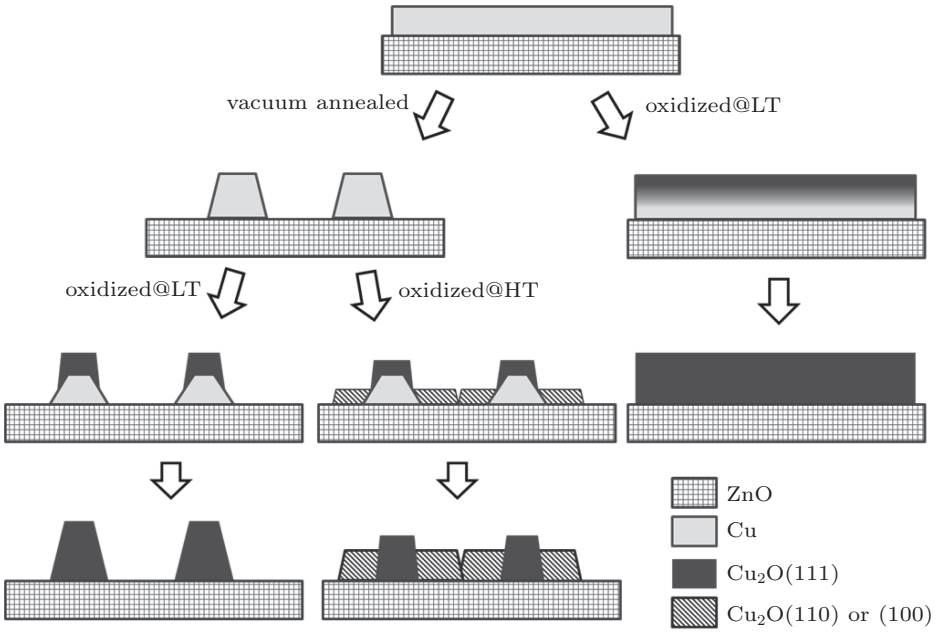


Fig. 6. Schematic illustration of the oxidation progress.

It should be noticed that the Cu_2O epitaxial film on ZnO (0001) has no (100) component both in our MBE experiments and other's MOCVD growth,[9] but it occurs in the oxidation results. The different growth conditions of oxidation are supposed to be responsible for the occurrence of this orientation. In the epitaxial growth experiments, the ZnO surface is protected by the oxygen plasma all the time before the Cu_2O deposition. However, in the high-temperature oxidation experiments, the ZnO surface is exposed in an ultrahigh vacuum before the oxidation and would decompose to some extent. The higher the temperature is, the more the surface degrades. So we assume that the emergence of Cu_2O (100) in the oxidized samples is related to the surface roughness of the partially decomposed ZnO. Note that in Fig. 2(a), the Cu_2O (100) peak does not emerge when Cu (111) is oxidized at 400 °C. That is because 400 °C is not high enough, so the ZnO surface only slightly decomposes. For the other samples oxidized at higher temperatures, the severer decomposition of ZnO leads to a quite rough surface providing nucleation centers for Cu_2O (100). To confirm our assumption, we oxidized the Cu film on a heavily Ga-doped ZnO layer at 400 °C, as it has a much rougher surface than the undoped ZnO even when the temperature is not so high. The morphologies of Cu_2O/ZnO and Cu_2O/ZnO:Ga are quite similar, but XRD θ–2θ scans (Fig. 7) show that

Cu_2O/ZnO:Ga oxidized at 400 °C is (100) dominated and the (110) component is dramatically suppressed.

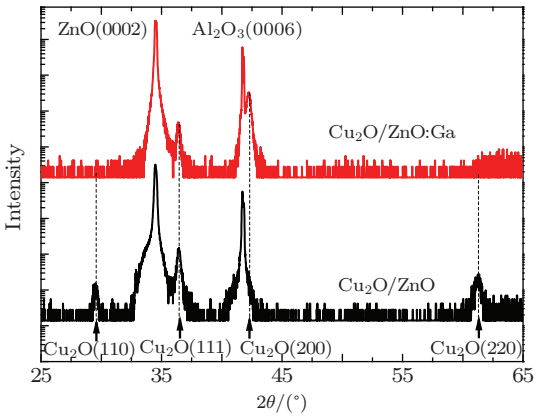


Fig. 7. (colour online) XRD θ–2θ scans of Cu_2O films oxidized at 400°C on ZnO:Ga and undoped ZnO templates.

4. Summary

In conclusion, the role of temperature on the oxidation dynamics of Cu_2O on ZnO (0001) was investigated with the assistance of oxygen plasma. At low temperatures, the oxidation followed a top-down vertical growth mechanism, resulting in a single crystalline Cu_2O (111) film with high quality. At high temperatures, however, a micro-zone phase separation of Cu_2O films was observed, and a lateral growth model was proposed to explain the underlying dynamics of this unique oxidation process. Both the vertical oxidation mode of Cu_2O (111) and the lateral oxidation mode of Cu_2O (110) and (100) were well supported by the experimental results, which clearly indicates the effect of oxidation temperature on the nucleation and growth dynamics of Cu_2O on ZnO (0001). The understanding of Cu oxidation behavior on ZnO is very important in broadening the science and physics research on copper oxides as well as in delicately controlling the crystal quality and microstructure of Cu_2O/ZnO heterojunction for technological applications.

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