Two-dimensional growth of continuous Cu_2O thin films by magnetron sputtering

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We present results on the *in situ*, two-dimensional growth (as opposed to the more commonly encountered island-coalescence mechanism) of continuous epitaxial Cu_2O films on MgO(011) using dc facing-magnetron sputtering from metallic Cu targets in an oxygen/argon atmosphere. Film growth was studied as a function of deposition time and the dc power applied to the guns. Control of the latter leads to either continuous or island-/rodlike film morphologies. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1861117]

Cuprous oxide (Cu_2O) has attracted much attention over the years. Some reasons for this interest involve its rather unique cuprite structure,[1] its importance in connection with the study of Bose–Einstein Condensation (BEC) of excitons,[2] and possible multilayer and superlattice devices applications.[3] Achieving BEC in a confined geometry, an interest of ours, may offer the opportunity to develop solid-state-based devices utilizing BEC related phenomena. Progress is now limited by difficulties associated with the preparation of high-quality films and for this reason the vast majority of optical investigations in the past have resorted to natural (geological) bulk crystals as an alternative.

In this letter, we report on the two-dimensional (2D) growth of continuous epitaxial Cu_2O thin films on MgO(011) single-crystal substrates by *in situ* facing-magnetron dc sputtering.[4] MgO was selected as the substrate because of its small lattice mismatch. Since the (011) orientation has been reported to be the most favorable for the epitaxial growth of Cu_2O,[5] we emphasized Cu_2O films grown on MgO(011), but, for comparison, we also show the results for Cu_2O films on MgO(001). Although there are several deposition parameters that can play important roles during the film growth, we here focus on only two of them: growth time and deposition rate. By increasing the growth time, we tracked the growth process; by adjusting the deposition rate, we could achieve two different morphologies of our Cu_2O films: continuous, and island-/rodlike.

Our experimental setup is rather simple: the chamber is a KWIK-FLANGE™ "Tee" (together with related components) while the components for the facing-magnetron guns were machined in our shop. In this system, the substrate was fastened to a heated substrate holder, the plane of which is perpendicular to a plane parallel to the two opposing metallic Cu targets. The distance between the Cu targets was 1 in. and each target is 1/2 in. in diameter. Three 3/8 in. diameter, 1/2 in. thick magnets are positioned in the tube directly behind each target (through which the cooling water flows). We remind the reader that the use of facing-magnetron guns minimizes the effect of resputtering of the growing film by the negative ion current known to be present in an oxygen plasma, while still achieving a high deposition rate; this should be contrasted with the often employed (especially in connection with oxide-based high T_c superconducting films) off-axes single-magnetron approach.

The chamber was evacuated with a turbo pump, which was backed by a mechanical pump, with a base pressure of about 10^{-5} Torr. Oxygen was used as the reactive gas component, combined with argon as the sputtering gas. Cu_2O formation may occur at: (1) the two target surfaces, (2) the substrate surface, or (3) in the plasma.[3] Based on the following important observation we suggest that the creation of Cu_2O mainly happens in a restricted region of the plasma: for certain combinations of the sputtering current, chamber pressure, and oxygen partial pressure we observe that red light is emitted from a confined region of the plasma. If the substrate is positioned adjacent to this red region the resulting films are Cu_2O rather than Cu or CuO [as judged by subsequent x-ray diffraction (XRD) studies]. In practice, for the best oxidation and effective sputtering, the distance between the substrate and the targets was approximately equal to the distance between the two targets. The substrate temperature varied from 690 °C to 750 °C.

In our experiments, the ratio of oxygen to argon plays a very important role. We find that a ratio of 1:16 yields both a reasonable sputtering rate and the desired oxidation state of Cu. Typically, the partial pressures of oxygen and argon were set at 2 mTorr and 32 mTorr, respectively. We note that, because the plasma promotes oxidation, the equilibrium phase diagram is not relevant in this environment: oxygen ions are clearly more reactive than molecular oxygen.[6]

Due to the lattice match noted above, and their modest cost, MgO(011) substrates (2-side polished and supplied by MTI Co., Richmond, CA) were used. We also used MgO(001) for comparison purposes.

The Cu_2O films we generated were red and transparent. They were analyzed with XRD, scanning electron microscopy (SEM), and atomic force microscopy (AFM).

The results from low-magnification optical images show that the Cu_2O films are red, continuous and optically smooth (shiny). We also did scratch tests. Comparing with those films deposited by the *ex situ* liquid-phase growth technique[7] and laser ablation, the Cu_2O films obtained by magnetron

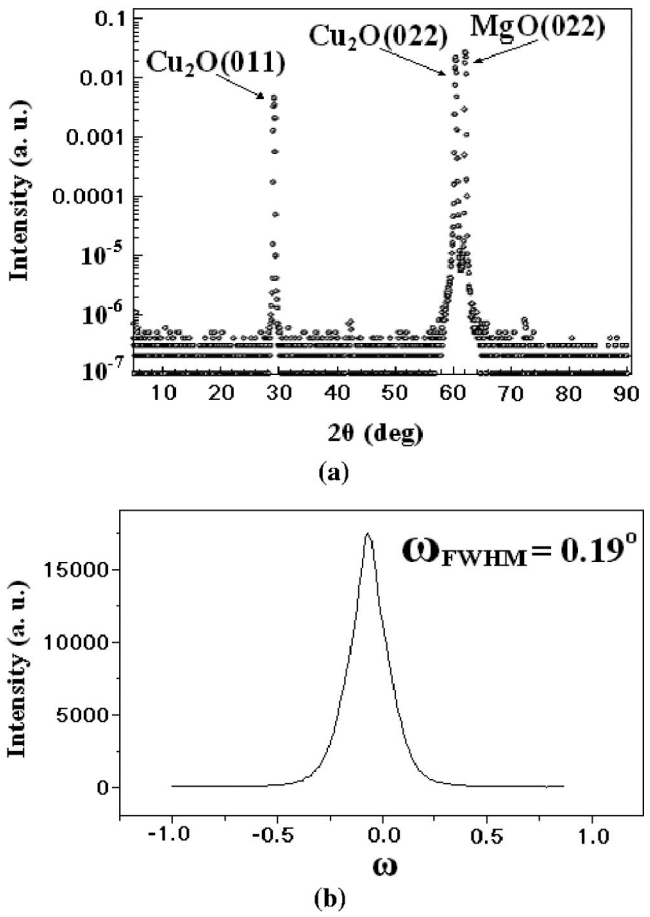

FIG. 1. XRD spectra of a Cu_2O film on MgO(011): (a) the θ–2θ diffraction trace; (b) the rocking curve of the Cu_2O(022) peak.

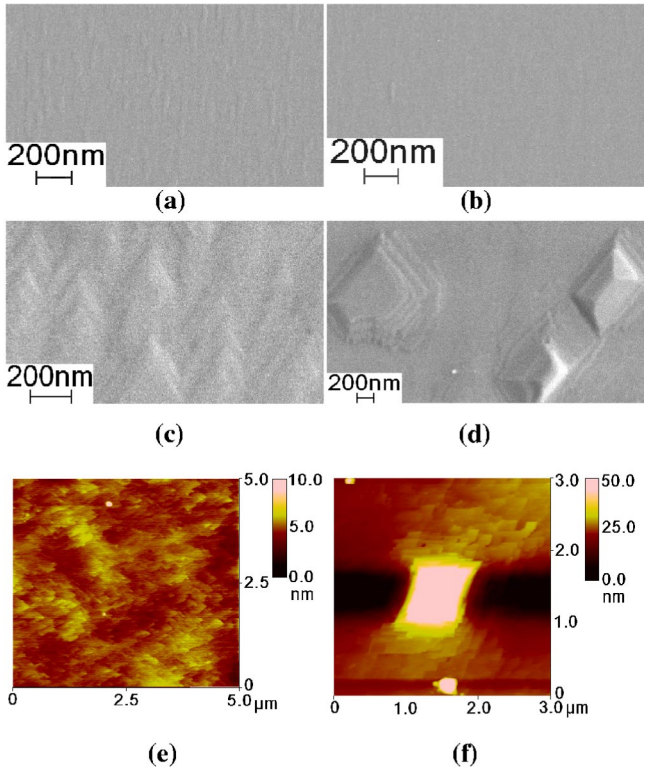

FIG. 2. SEM and AFM images of a Cu_2O film on MgO(011) deposited at a rate of ~0.02 μm per min for different growth times of: (a)–(d) SEM results of 10, 20, 30, and 40 min, respectively; (e), (f) AFM results of 20 and 40 min, respectively.

sputtering are functionally much harder, i.e., much more difficult to be scratched and removed from the MgO substrates. This indicates that a denser film with better adhesion to the substrate has been synthesized. The improvement on the film hardness and adhesion may be due to the higher kinetic energy of sputtered particles (2–30 eV) (Ref. 8) compared to the thermal energy (0.1 eV) provided by the high growth temperature of 1180 °C in the liquid-phase growth.[7] Although further characterization would be desirable, we believe that the qualitative improvement achieved in the hardness of our Cu_2O films is relevant to the evolution of device quality material.

Figure 1(a) shows the result of an XRD θ–2θ scan of a Cu_2O film on MgO(011), which was deposited at 700 °C with a deposition rate of ~0.02 μm per min, and a growth time of 20 min. The presence of the Cu_2O(011), (022) peaks along with the MgO(022) peak verifies that the Cu_2O film is highly crystalline with a single orientation. The XRD data also reveals that the Cu_2O(022) peak is shifted approximately 0.5° lower than the expected 61.334° position for bulk Cu_2O. This shift corresponds to the expansion of the film in the out-of-plane lattice spacing, which suggests that the film has an in-plane compression due to the lattice mismatch between the Cu_2O film and MgO substrate. A similar phenomenon was observed from the Cu_2O film made by the high temperature (1118 °C) liquid-phase growth,[7] although the growth temperature here was much lower. Figure 1(b) illustrates the rocking curve of the (022) peak, which has a FWHM of 0.19°, indicating the excellent crystallinity. As mentioned above, the substrate temperature varied from 690 °C to 750 °C, but based on the data we collected it seems that the quality of the film is not sensitive to the substrate temperature in this range.

Figures 2(a)–2(f) show the SEM and the AFM results for Cu_2O films on MgO(011) with growth times of 10 min, 20 min, 30 min, and 40 min, respectively. SEM images reveal that the surfaces of the films are flat and continuous for growth times up to 20 min [Figs. 2(a) and 2(b)]. A closer examination by AFM on the film with a growth time of 20 min [Fig. 2(e)] shows terrace structures on the surface, which is characteristic of 2D growth. 3D island growth of Cu_2O has been observed in metalorganic chemical vapor deposition,[9] while our results show that 2D continuous films can be grown using magnetron sputtering. The 2D growth is aided by the energetic particle bombardment in the sputtering growth. The energetic particle bombardment may affect the nucleation kinetics and hence result in the 2D growth through several mechanisms such as: increased adsorption sites, enhanced adatom diffusion, preferential sputtering from 3D islands, etc.[10] However, we also noticed that the global 2D growth trend (across the entire substrate) deteriorated when the growth time was prolonged, as shown in Figs. 2(c) and 2(d). Islands are found to appear on the surface, while both the SEM [Figs. 2(c) and 2(d)] and AFM images [Fig. 2(f)] show the 2D terrace structure of these islands indicating the island growth still follows the 2D mode. Based on these results, we conclude that the growth of our continuous Cu_2O films on MgO(011) results from a 2D mode, rather than initiating as an ensemble of nucleated islands which then coalesce;[9] after a critical thickness of approximately 0.4 μm, 2D island growth occurs. The 2D island growth here

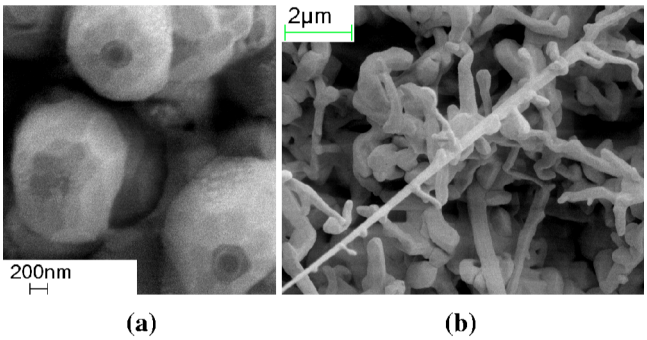

FIG. 3. SEM images of a Cu_2O film on MgO(011) deposited at a rate of ~0.01 μm per min: (a) island-like; (b) rod-like.

has three major characteristics: (1) It has a large critical thickness of 0.4 μm for island growth rather than several monolayers; (2) The islands are 2D in our case rather than 3D; (3) XRD analysis reveals that there is no significant position shift of the $Cu_2O(022)$ peaks before and after the appearance of the islands. Thereafter, the 2D island growth in our experiments does not result from the strain energy relaxation. However, the transition from the continuous film growth to 2D island growth is not completely understood.

By adjusting the dc power supplied to the guns, which in turn affects the number and to some extent the energy of the impacting Cu atoms/ions, we observe a change in the morphology of the Cu_2O films: with a high deposition rate (~0.02 μm per min) we obtain the continuous film seen in Fig. 2; while, with a slower deposition rate (~0.01 μm per min) we obtain "islandlike" [Fig. 3(a)] or "rodlike" [Fig. 3(b)] morphologies. However, from our experiments, we found that there was a range of deposition rates for the successful growth of single phase Cu_2O material. If the deposition rate is higher than 0.025 μm per min, metallic Cu peaks appear in the XRD results; if it is lower than 0.005 μm per min, CuO peaks are observed.

By comparison, Cu_2O films grown on MgO(001) substrates are also red, smooth (shiny), and transparent. Figure 4(a) shows the XRD result for a Cu_2O film on (001), prepared with the same deposition parameters as used for the (011) film shown in Fig. 2. The Cu_2O film on MgO(001) displays three different crystal orientations: (111), (011), and (001). From Fig. 4(a), we see that the intensity of (111) peak is very weak. Although the intensity of (002) is quite high, after accounting for the intrinsic difference between the bulk (011) and (002) intensities, the normalized intensity of (011) line is actually about 70 times stronger than that for the (002). Thus, in spite of the fact that growth is on a (001) substrate, the natural tendency toward (011) growth dominates.[5] Figure 4(b) shows the SEM results of a film on MgO(001). Based on all data collected, we conclude that reasonably high quality Cu_2O thin films can also be generated on MgO(001). When considering the lower cost of MgO(001) [in comparison with MgO(011)] it should continue to receive attention.

We have shown that facing-magnetron, reactive-sputtering of metallic Cu on MgO(011) substrates can yield continuous, single-crystal-like, epitaxial Cu_2O films *in situ*,

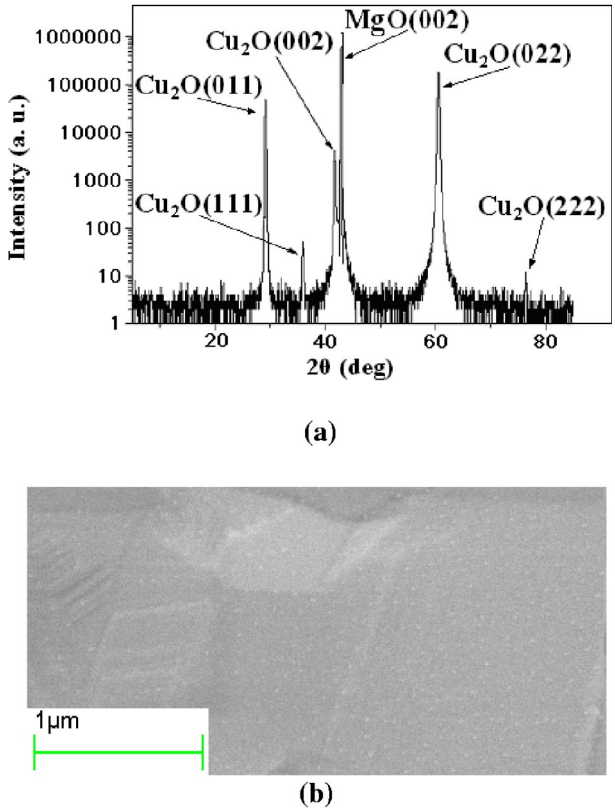

FIG. 4. (a) θ–2θ XRD spectrum of a Cu_2O film on MgO(001); (b) SEM image of a Cu_2O film on MgO(001).

which grow in a 2D mode. To the best of our knowledge, we believe this is the first observation of high quality Cu_2O film growth on MgO to be obtained by an *in situ* sputtering method. Our experimental setup is rather simple, and the various procedures are easy to control.

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