Single phase, single orientation Cu$_2$O (1 0 0) and (1 1 0) thin films grown by plasma-assisted molecular beam epitaxy

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Epitaxial growth of cuprous oxide (Cu$_2$O) has been achieved on (1 0 0) and (1 1 0) orientations of MgO by plasma-assisted molecular beam epitaxy. Growth was investigated using a pure oxygen plasma as well as a 90%Ar/10%O$_2$ plasma. Cu$_2$O films grown using pure oxygen on MgO (1 0 0) have a limited growth window and typically exhibit multiple phases and orientations. Films grown on MgO (1 1 0) using pure oxygen are phase stable and predominantly (1 1 0) oriented, with some (2 0 0) orientation present. Films grown using an Ar/O$_2$ plasma on MgO (1 0 0) have improved phase stability and a single (1 1 0) orientation. Growth on MgO (1 1 0) using an Ar/O$_2$ plasma yields highly reproducible (1 1 0) oriented single phase Cu$_2$O films with a much wider growth window, suggesting that this substrate orientation is preferable for Cu$_2$O phase stability.

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1. Introduction

Cuprous oxide (Cu$_2$O) was one of the first semiconductors to be studied, and many of its bulk properties have since been elucidated. In the past few decades, Cu$_2$O gained attention as an earth-abundant semiconductor with promising photovoltaic properties including high absorption and long minority carrier diffusion length around 5 μm [1,2]. It is composed of non-toxic elements and can be easily fabricated by thermal oxidation of Cu foils. While the bulk properties of Cu$_2$O are attractive for photovoltaic applications, surface stability has been one of the most pressing issues to achieve a high efficiency solar cell. Cu$_2$O is intrinsically p-type and thus requires a heterojunction partner to form a solar cell with a high open circuit voltage, which introduces the possibility of heterojunction interface defects. Cu$_2$O devices are highly susceptible to deleterious interface reactions which impede high cell performance [3,4]. The highest reported photovoltaic efficiency for a Cu$_2$O absorber device is 5.38% [5], while the detailed balance limit has been calculated to exceed 20% [1]. One of the main reasons for low efficiency is phase instability of the Cu$_2$O surface, coupled with a small heat of formation (∆H = 170 kJ/mol) and a low electron affinity (3.2 eV). A thermodynamic phase diagram for the Cu–O system can be found in [2].

Arguably the strongest motivation for Cu$_2$O in photovoltaic applications is its relatively large band gap of 2.1 eV (and exciton gap at 1.9 eV), which make it a promising candidate as a top cell in a tandem solar cell combined with a crystalline silicon bottom cell. In order for such a tandem cell to improve upon existing Si cell efficiency, a Cu$_2$O cell efficiency approaching 10% is required [6]. The development of such a structure would require synthesis by thin film methods, and molecular beam epitaxy (MBE) provides precise control over many deposition parameters and generally yields high quality material. MBE synthesis of Cu$_2$O on MgO substrates has been demonstrated using pure atomic oxygen [7–9], however no reports of a diluted oxygen plasma have been made to date. Also, growth on MgO (1 1 0) surface has been reported by sputtering [10] and pulsed laser deposition [11], but not by MBE. DFT calculations [12] show that the Cu$_2$O (1 1 0) surface has the lowest energy, so it is reasonable to assume that a substrate that promotes growth in this direction may foster Cu$_2$O phase stability over a larger range of deposition parameters, and this is consistent with results of this work. We compare the structural properties of Cu$_2$O films grown using a pure oxygen atmosphere to films grown using a 90%Ar/10%O$_2$ premix, on (1 0 0) and (1 1 0) orientations of MgO.

2. Experimental details

Thin films of Cu$_2$O were grown in a custom molecular beam epitaxy system equipped with an Oxford RF atom source. RF atom sources dissociate molecular species (such as O$_2$ or N$_2$) into atomic species for increased reactivity while minimizing ionic species...
which typically have high kinetic energies and are associated with creation of point defects. Ionic components of the plasma that escape the atom source were further filtered out by ion deflection plates. Thus the current of gas species was composed of atomic argon and/or oxygen. Oxygen (Air Liquide, 99.9999% purity) partial pressure was varied between $1 \times 10^{-7}$ and $1 \times 10^{-5}$ Torr. For growths with argon/oxygen premix (Air Liquide, 99.9999% purity, 10.0% oxygen, balance argon), the gas partial pressure of argon was correspondingly an order of magnitude higher. The presence of argon allowed for stability of the plasma, while decreasing the partial pressure of reactive oxygen species. Partial pressures were monitored by a residual gas analyzer (RGA). Atom source plasma power was varied between 100 and 200 W and plasma optical emission voltage ranged from 1 V to 3 V during film deposition. Plasma emission voltage corresponds to the intensity of light emitted from the plasma and correlates with the efficiency of dissociation of the molecular gas into its atomic components. The growth chamber base pressure was $< 3 \times 10^{-9}$ Torr. Copper metal (6 N, Alfa Aesar) was evaporated from a high temperature effusion cell at a temperature ranging from 1250 to 1300 °C. Cu$_2$O was formed reactively at the surface of the substrate kept at a temperature ranging from 400 to 650 °C. MgO was chosen as a substrate because it is the closest lattice matched commercially available single crystal; it is also refractory, transparent, and non-conductive, which makes it suitable for a variety of electrical and optical characterization techniques. MgO substrates were cleaned in situ by annealing at deposition temperature for an hour and subsequently plasma cleaned for 10 minutes. In situ reflection high energy electron diffraction (RHEED, with electron beam energy of 15 keV) was used to confirm cleanliness and orientation of the substrate surface and monitor film structure at various stages of the growth. Ex situ characterization included high resolution X-ray diffraction (HRXRD, Panalytical X Pert Pro), transmission electron microscopy (TEM, FEI Tecnai F30 with S-TWIN objective, 300 keV electron energy), and atomic force microscopy (AFM, Asylum Research MFP 3D). TEM cross sections were prepared using standard focused ion beam milling on an FEI Versa 3D.

3. Results and discussion

3.1. Growth using pure oxygen plasma

Growth of Cu$_2$O on MgO was initially studied by varying oxygen partial pressure (using pure oxygen gas) and substrate temperature, while fixing the Cu effusion cell temperature at 1275 °C, atom source plasma power at 100 W, and plasma optical emission voltage at 1 V (which corresponds to the lower range of stability of the plasma source). As illustrated in Fig. 1(a, b), the growth window for the Cu$_2$O phase on MgO (1 0 0) was found to be too

**Fig. 1.** HRXRD spectra of Cu$_2$O films grown on MgO (1 0 0) at (a) $1 \times 10^{-6}$ Torr and (b) $5 \times 10^{-6}$ Torr oxygen, both cases corresponding to the presence of undesirable phases and (c) pure phase Cu$_2$O film grown on MgO (1 1 0) at $9 \times 10^{-6}$ Torr.

**Fig. 2.** RHEED images of Cu$_2$O growth on MgO using pure oxygen plasma. (a) Plasma cleaned MgO (1 0 0) surface along the [1 1 0] azimuth; (b) 100 nm of Cu$_2$O showing growth initiates and persists in the Volmer–Weber or island regime and the pattern is a superposition of the Cu$_2$O [1 1 0] and [2 1 1] zone axis transmission patterns; (c) indexing of diffraction spots in (b) along [1 1 0] zone axis (black) and [2 1 1] zone axis (gray); (d) plasma cleaned MgO (1 1 0) surface along the [1 1 1] azimuth; (e) 10 nm of Cu$_2$O along [1 1 1] again initiates with island growth (for spot indexing refer to Fig. 5f); (f) after 100 nm of Cu$_2$O viewed along [1 1 1], islands merge into a smooth film with steps, as evidenced by a streaky pattern.
narrow to reproducibly grow single phase films. Raising the pressure of oxygen by only half an order of magnitude, while maintaining otherwise identical growth parameters and low oxygen plasma power, changed the film composition from a mixture of Cu$_2$O and Cu to CuO. Fig. 1(c) shows that single-phase epitaxial growth of Cu$_2$O on MgO (1 1 0) is achievable within a narrow range of deposition parameters using pure oxygen. It should be noted that using pure oxygen, two orientations of Cu$_2$O, namely the (1 1 0) and (2 0 0), are commonly present.

The difficulty of growing single phase, single orientation Cu$_2$O on MgO (1 0 0) has been demonstrated before, and it is known that the (1 1 0) MgO orientation is more amenable to unidirectional Cu$_2$O epitaxy, and regardless of substrate orientation, growth of Cu$_2$O in the (1 1 0) direction is usually preferred compared to (1 0 0). Although reasons for this are still debated and different epitaxial relationships have been reported [7,8,13,14], density functional theory calculations show that the Cu$_2$O (1 1 0):CuO surface has the lowest energy, and generally the nonpolar Cu$_2$O (1 1 0) surfaces have lower energies than the polar Cu$_2$O (1 0 0) surfaces [12]. Lattice mismatch seems to be less important than surface energy in determining the preferential growth direction [7].

Fig. 2(a)–(c) shows RHEED patterns for growth of Cu$_2$O on MgO (1 0 0). Growth of Cu$_2$O initiates with islands corresponding to two symmetrically equivalent variants of the Cu$_2$O (1 1 0) surface such that the pattern in Fig. 2b is a superposition of the Cu$_2$O [1 1 0] and [2 1 1] zone axis transmission patterns. Fig. 2c shows the schematic indexing of the diffraction spots. These results are consistent with the literature results of Cu$_2$O growth on MgO (1 0 0) [7,14]. Fig. 2(d)–(f) shows that growth of Cu$_2$O on MgO (1 1 0) starts in the Volmer–Weber or island regime, and the islands eventually merge to form a smooth and continuous film with some surface disorder as evidenced by the streaky nature of the pattern [15]. Note that the RHEED pattern corresponds to only a single orientation of the film, which indicates that nucleation of the second orientation is not spatially uniform and most likely predominates away from the center of the sample.

Despite some success in growing single phase Cu$_2$O films on the (1 1 0) MgO orientation, reproducibility was still an issue due to the limited oxygen partial pressure growth window. The partial pressure of oxygen needed to produce a stable plasma in the RF atom source needed to exceed 1 x 10^{-6} Torr, and the growth window for pure Cu$_2$O was found to be close to this limit for pure oxygen. There are several ways to enable growth of single phase, single crystalline orientation Cu$_2$O, which include raising substrate temperature, raising the Cu flux, and using a different oxidant. The substrate temperature was already approaching the limits of the system, and higher growth temperature is generally undesirable in terms of substrate compatibility and cost. Raising the Cu flux by increasing

![HRXRD spectra of Cu$_2$O grown on (a) MgO (1 0 0) and (b) MgO (1 1 0) using argon–oxygen plasma. Spectra are labeled with deposition temperature, plasma power, and plasma optical emission voltage.](image1)

![MBE regime phase diagram for growth of Cu$_2$O on (a) MgO (1 0 0) and (b) MgO (1 1 0), using argon–oxygen plasma.](image2)
source filament temperature is also problematic in terms of operation costs and effusion cell lifetime. Instead, oxygen partial pressure was diluted using an inert balance gas (90%Ar/10%O2 premix) to enable plasma stability at lower oxygen partial pressures.

3.2. Growth using 90%Ar/10%O2 plasma

Fig. 3 shows HRXRD data of various films of Cu2O grown on (a) MgO (1 0 0) and (b) MgO (1 1 0). The XRD peak intensities

Fig. 5. RHEED images of Cu2O growth on MgO using argon–oxygen plasma. (a) Plasma cleaned MgO (1 0 0) surface along the [1 1 0] azimuth; (b) 60 nm of Cu2O proceeds with island growth shown here along the [1 0 0] azimuth, and islands start to merge into a smooth film, as evidenced by the appearance of streaks, but growth remains 3-dimensional, which may be attributed to lower film thickness than in the pure oxygen films. (c) Schematic spot indexing along [100] zone axis of Cu2O; (d) plasma cleaned MgO (1 1 0) surface along the [1 1 1] azimuth; (e) 60 nm of Cu2O shown here along the [1 1 1] azimuth showing growth initiates and persists in the island regime; (f) schematic spot indexing along the [1 1 1] zone axis of Cu2O.

Fig. 6. (a) AFM image of a 20 nm Cu2O film grown on MgO (1 1 0) using an argon–oxygen plasma showing island-type film morphology. (b) TEM micrograph showing cross sectional morphology of Cu2O on MgO (1 1 0) confirming island-growth regime.

Fig. 7. (a) High resolution cross-sectional TEM of (1 1 0) Cu2O on MgO (1 1 0) viewed down the [1 1 1] zone axis shows epitaxial relationship between film and substrate. (b) Selected area electron diffraction pattern shows a superposition of the Cu2O [1 1 1] and MgO [1 1 1] zone axis diffraction patterns, confirming epitaxial relationship. Note the presence of amorphous rings due to Pt protective layer.
are lower compared to those of Fig. 1 because film thickness is substantially reduced using a 90% Ar/10% O₂ gas mixture. Growth rate using pure oxygen at 550 °C was measured by X-ray refection to be 100 nm/h, while growth using the Ar/O₂ gas mixture was measured to be 20 nm/h.

For growth on MgO (1 0 0), Cu₂O films are obtained at low plasma optical voltages and powers, and intermediate substrate temperatures. Plasma emission voltage, which is a function of gas flow rate and plasma power, was found to better correlate with the epitaxial film quality than either the gas flow rate or the plasma power. The epitaxial growth phase diagram in Fig. 4a summarizes these results. As shown in Fig. 3b, films grown on MgO (1 1 0) all have a single orientation in the (1 1 0) Cu₂O direction, for a wide range of plasma parameters and substrate temperatures.

Fig. 5(a)–(c) shows representative RHEED patterns for pure Cu₂O grown on MgO (1 0 0); growth starts in the Volmer–Weber island growth mode and after 60 nm starts to smooth out into a continuous film as evidenced by the appearance of streaks. Growth on the MgO (1 1 0) surface is shown in Fig. 5(d)–(f). In contrast to films grown using pure oxygen that exhibited two variants of the Cu₂O (1 1 0) orientation, films grown using Ar/O₂ exhibit only one variant, at least within the region probed by the RHEED electron beam. Looking at the [1 1 1] Cu₂O azimuth in Fig. 5e, all spots can be indexed to the corresponding transmission diffraction pattern shown in Fig. 5f, and no extra spots corresponding to the [2 1 1] azimuth are present. The pattern looks very similar to that of Fig. 2e. Growth remains 3-dimensional possibly due to the fact that the film thickness is not large enough to completely cover the MgO surface, as seen in AFM and TEM examination of the film in Fig. 6. The epitaxial relationship of Cu₂O (1 1 0) on MgO (1 1 0) was confirmed directly by TEM, as shown in Fig. 7. The selected area diffraction pattern in Fig. 7b shows that the Cu₂O lattice directly overlaps the MgO lattice and the film appears to be strained.

4. Conclusion

Single phase, single orientation Cu₂O thin films have been grown on MgO by plasma-assisted molecular beam epitaxy using both pure oxygen and argon–oxygen gas mixtures. Growth using argon–oxygen opens up the stability window of the Cu₂O phase by giving access to lower partial pressures of oxygen while still maintaining a stable plasma. The film growth rate using argon–oxygen is reduced compared to pure oxygen; however film mosaicity and texture are also reduced, yielding a film with increased crystallinity. The results of this work facilitate the development of high quality absorber layers for an epitaxial Cu₂O solar cell device.

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