Journal of Crystal Growth 410 (2015) 77–81

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Single phase, single orientation Cu_2O (1 0 0) and (1 1 0) thin films grown by plasma-assisted molecular beam epitaxy

Yulia Tolstova *, Samantha S. Wilson, Harry A. Atwater

Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Pasadena, CA 91125, United States

ARTICLE INFO

Article history:
Received 16 July 2014
Received in revised form
15 October 2014
Accepted 21 October 2014
Communicated by R. Fornari
Available online 30 October 2014

Keywords:
A1. Crystal structure
A1. High resolution X-ray diffraction
A3. Molecular beam epitaxy
B1. Oxides
B2. Semiconducting materials

ABSTRACT

Epitaxial growth of cuprous oxide (Cu_2O) 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_2O 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_2O films with a much wider growth window, suggesting that this substrate orientation is preferable for Cu_2O phase stability.

1. Introduction

Cuprous oxide (Cu_2O) 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_2O 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_2O are attractive for photovoltaic applications, surface stability has been one of the most pressing issues to achieve a high efficiency solar cell. Cu_2O 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_2O devices are highly susceptible to deleterious interface reactions which impede high cell performance [3,4]. The highest reported photovoltaic efficiency for a Cu_2O 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_2O surface, coupled with a small heat of formation (-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_2O 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_2O 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_2O 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_2O (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_2O 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_2O 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_xO 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

* Corresponding author.
E-mail address: yulia@caltech.edu (Y. Tolstova).

http://dx.doi.org/10.1016/j.jcrysgro.2014.10.045
0022-0248/

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 1×10^{-7} and 1×10^{-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 $<3\times10^{-9}$ 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_xO 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 XPert 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_xO 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_2O phase on MgO (1 0 0) was found to be too

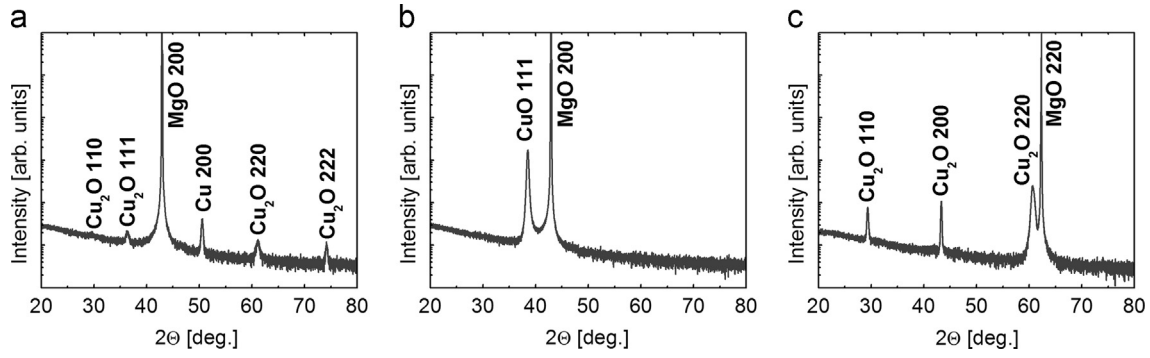

Fig. 1. HRXRD spectra of Cu_xO films grown on MgO (1 0 0) at (a) 1×10^{-6} Torr and (b) 5×10^{-6} Torr oxygen, both cases corresponding to the presence of undesirable phases and (c) pure phase Cu_2O film grown on MgO (1 1 0) at 9×10^{-6} Torr.

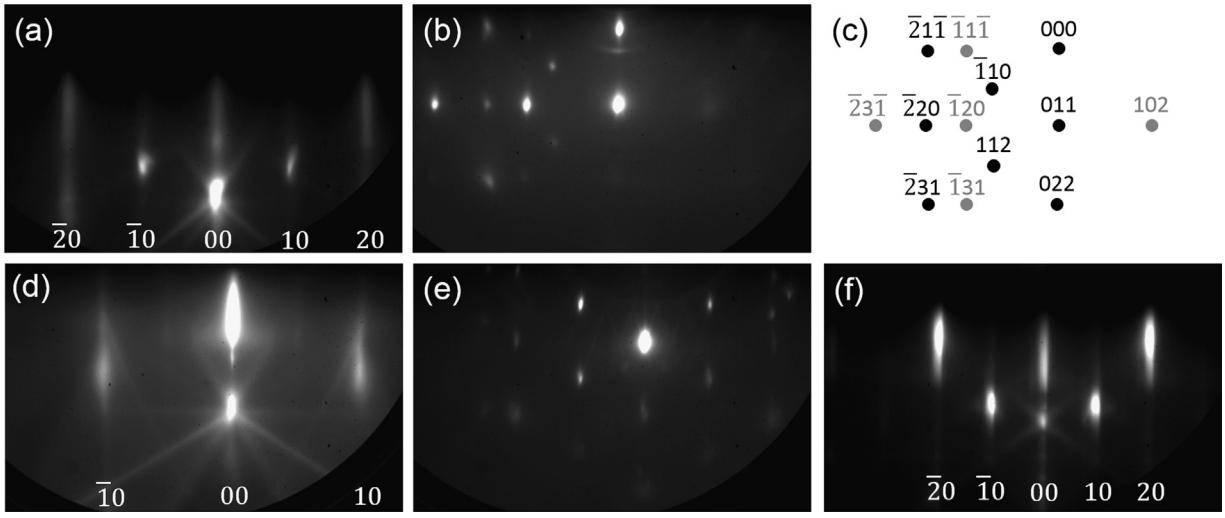

Fig. 2. RHEED images of Cu_2O growth on MgO using pure oxygen plasma. (a) Plasma cleaned MgO (1 0 0) surface along the [1 1 0] azimuth; (b) 100 nm of Cu_2O showing growth initiates and persists in the Volmer–Weber or island regime and the pattern is a superposition of the Cu_2O [1 1 $\bar{1}$] and [2 1 $\bar{1}$] zone axis transmission patterns; (c) indexing of diffraction spots in (b) along [1 1 $\bar{1}$] zone axis (black) and [2 1 $\bar{1}$] zone axis (gray); (d) plasma cleaned MgO (1 1 0) surface along the [1 1 1] azimuth; (e) 10 nm of Cu_2O along [1 1 $\bar{1}$] again initiates with island growth (for spot indexing refer to Fig. 5f); (f) after 100 nm of Cu_2O viewed along [1 1 $\bar{1}$], 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_2O and Cu to CuO. Fig. 1(c) shows that single-phase epitaxial growth of Cu_2O 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_2O, namely the (1 1 0) and (2 0 0), are commonly present.

The difficulty of growing single phase, single orientation Cu_2O 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_2O epitaxy, and regardless of substrate orientation, growth of Cu_2O 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_2O (1 1 0):CuO surface has the lowest energy, and generally the nonpolar Cu_2O (1 1 0) surfaces have lower energies than the polar Cu_2O (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_2O on MgO (1 0 0). Growth of Cu_2O initiates with islands corresponding to two symmetrically equivalent variants of the Cu_2O (1 1 0) surface such that the pattern in Fig. 2b is a superposition of the Cu_2O [1 1 $\bar{1}$] and [2 1 $\bar{1}$] zone axis transmission patterns. Fig. 2c shows the schematic indexing of the diffraction spots. These results are consistent with the literature results of Cu_2O growth on MgO (1 0 0) [7,14]. Fig. 2(d)-(f) shows that growth of Cu_2O 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_2O 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 1×10^{-6} Torr, and the growth window for pure Cu_2O 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_2O, 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

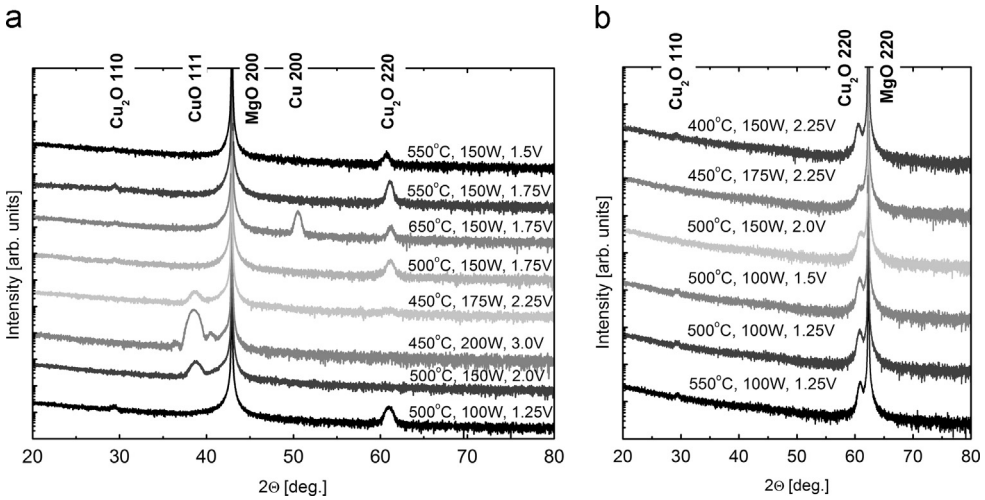

Fig. 3. HRXRD spectra of Cu_xO grown on (a) MgO (1 0 0) and (b) MgO (1 1 0) using argon–oxygen plasma. Spectra are labeled with deposition temperature, plasma power, and plasma optical emission voltage.

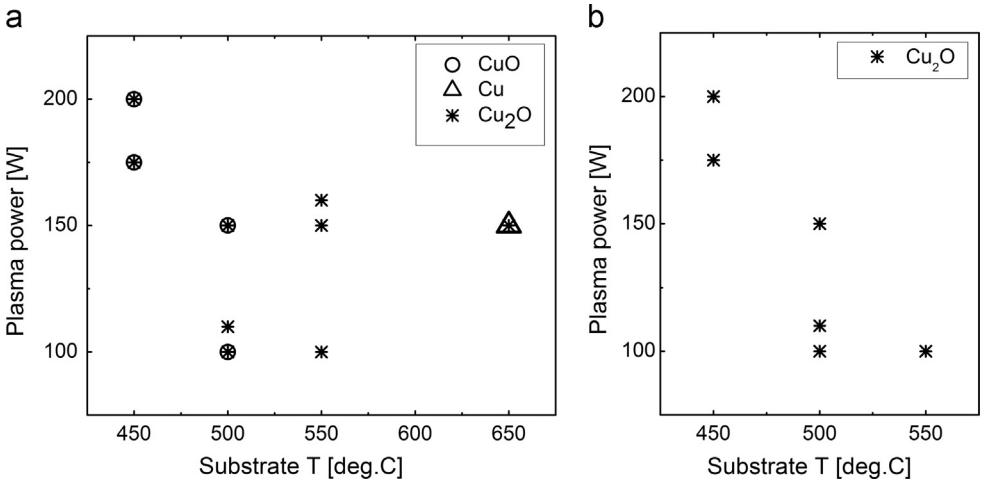

Fig. 4. MBE regime phase diagram for growth of Cu_xO on (a) MgO (1 0 0) and (b) MgO (1 1 0), using argon–oxygen plasma.

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%O_2 premix) to enable plasma stability at lower oxygen partial pressures.

3.2. Growth using 90%Ar/10%O_2 plasma

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

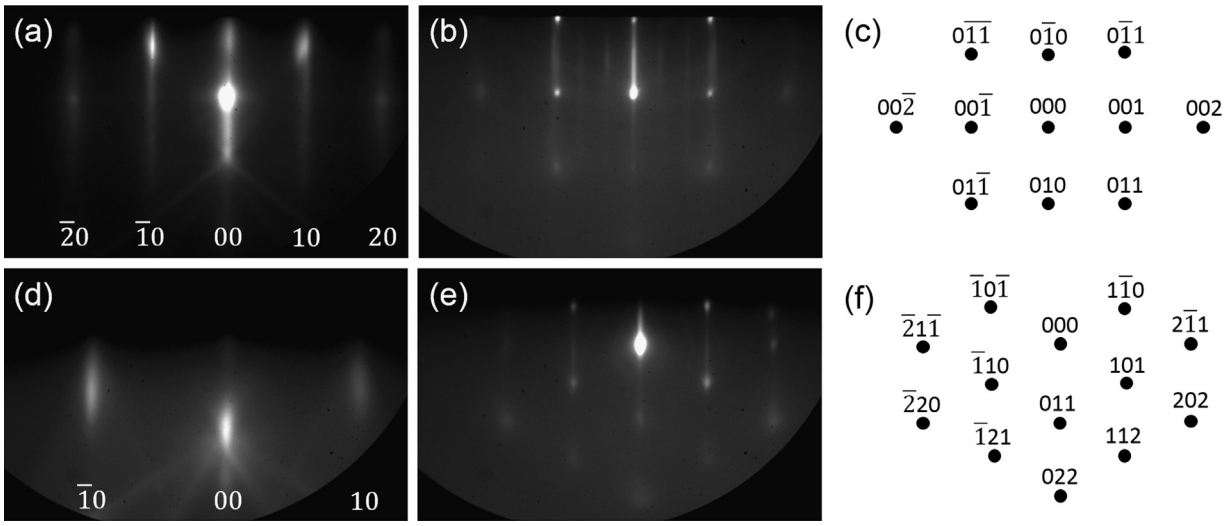

Fig. 5. RHEED images of Cu_2O growth on MgO using argon–oxygen plasma. (a) Plasma cleaned MgO (1 0 0) surface along the [1 1 0] azimuth; (b) 60 nm of Cu_2O proceeds with island growth shown here along the [1 0 0] azimuth, and islands start to merge into a smooth film, as evidenced by the appearance of 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 Cu_2O; (d) plasma cleaned MgO (1 1 0) surface along the [1 1 1] azimuth; (e) 60 nm of Cu_2O shown here along the [1 1 $\bar{1}$] azimuth showing growth initiates and persists in the island regime; (f) schematic spot indexing along the [1 1 $\bar{1}$] zone axis of Cu_2O.

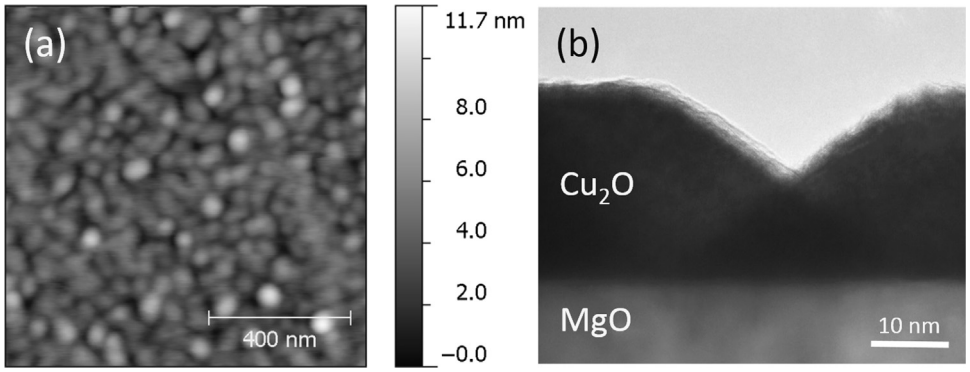

Fig. 6. (a) AFM image of a 20 nm Cu_2O film grown on MgO (1 1 0) using an argon–oxygen plasma showing island-type film morphology. (b) TEM micrograph showing cross sectional morphology of Cu_2O on MgO (1 1 0) confirming island-growth regime.

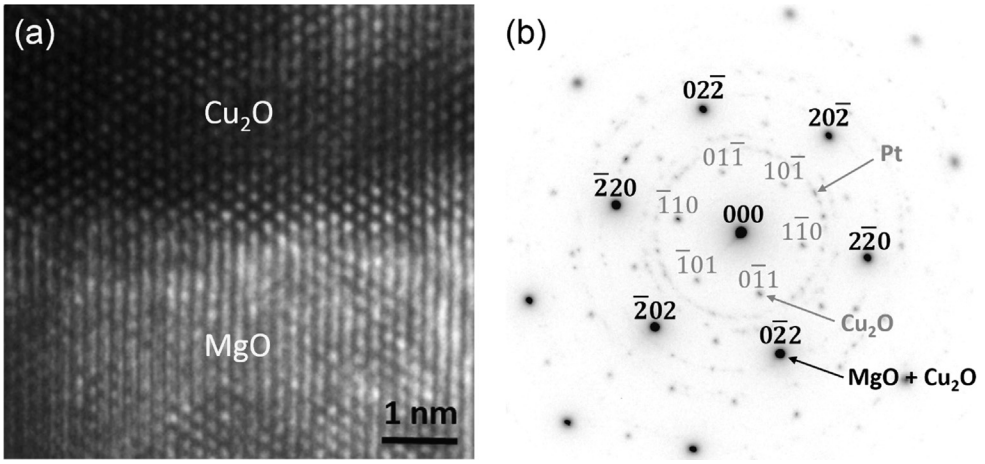

Fig. 7. (a) High resolution cross-sectional TEM of (1 1 0) Cu_2O on MgO (1 1 0) viewed down the [1 1 1] zone axis shows epitaxial relationship between film and substrate. (b) Selected area electron diffraction pattern shows a superposition of the Cu_2O [1 1 1] and MgO [1 1 1] zone axis diffraction patterns, 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%O_2 gas mixture. Growth rate using pure oxygen at 550 °C was measured by X-ray reflectivity to be 100 nm/h, while growth using the Ar/O_2 gas mixture was measured to be 20 nm/h.

For growth on MgO (1 0 0), Cu_2O 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) Cu_2O direction, for a wide range of plasma parameters and substrate temperatures.

Fig. 5(a)–(c) shows representative RHEED patterns for pure Cu_2O 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 Cu_2O (1 1 0) orientation, films grown using Ar/O_2 exhibit only one variant, at least within the region probed by the RHEED electron beam. Looking at the [1 1 $\bar{1}$] Cu_2O 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 $\bar{1}$] 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 Cu_2O (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 Cu_2O lattice directly overlaps the MgO lattice and the film appears to be strained.

4. Conclusion

Single phase, single orientation Cu_2O 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 Cu_2O 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 Cu_2O solar cell device.

Acknowledgments

The authors gratefully acknowledge support from the Dow Chemical Company under the earth abundant semiconductor project, as well as Carol Garland for TEM training and helpful assistance.

References

[1] L.C. Olsen, F.W. Addis, W. Miller, Solar Cells 7 (1982) 247–279.
[2] A.E. Rakhshani, Solid-State Electron. 29 (1986) 7–17.
[3] S.S. Wilson, J.P. Bosco, Y. Tolstova, D.O. Scanlon, G.W. Watson, H.A. Atwater, Energy Environ. Sci. 7 (2014) 3606–3610.
[4] S.W. Lee, Y.S. Lee, et al., Adv. Energy Mater. (2014) 1301916.
[5] T. Minami, Y. Nishi, T. Miyata, Appl. Phys. Express 6 (2013) 044101.
[6] T.P. White, N.N. Lal, K.R. Catchpole, IEEE J. Photovolt. 4 (2014) 208–214.
[7] K. Kawaguchi, R. Kita, M. Nishiyama, T. Morishita, J. Cryst. Growth 143 (1994) 221–226.
[8] D.S. Darvish, H.A. Atwater, J. Cryst. Growth 319 (2011) 39–43.
[9] J. Li, Z. Mei, D. Ye, H. Liang, Y. Liu, X. Du, J. Cryst. Growth 353 (2012) 63–67.
[10] Z.G. Yin, H.T. Zhang, D.M. Goodner, M.J. Bedzyk, R.P.H. Change, Y. Sun, J.B. Ketterson, Appl. Phys. Lett. 86 (2005) 061901.
[11] K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, H. Hosono, Appl. Phys. Lett. 93 (2008) 202107.
[12] A. Soon, M. Todorova, B. Delley, C. Stampfl, Phys. Rev. B 75 (2007) 125420.
[13] W. Seiler, E. Millon, J. Perriere, R. Benzerga, C. Boulmer-Loborgne, J. Cryst Growth 311 (2009) 3352–3358.
[14] Y. Fu, H. Lei, X. Wang, et al., Appl. Surf. Sci. 273 (2013) 19–23.
[15] A. Ichimiya, P.I. Cohen, Reflection High Energy Electron Diffraction, Cambridge University Press, Cambridge, United Kingdom, 2003.