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Epitaxial growth of Cu_2O and ZnO/Cu_2O thin films on MgO by plasma-assisted molecular beam epitaxy

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ABSTRACT

We report the epitaxial growth of Cu_2O (0 0 1) and *m*-plane (1 0 $\bar{1}$ 0) ZnO/Cu_2O thin films on both bulk MgO (0 0 1) and biaxially textured thin films of MgO (0 0 1) via plasma-assisted molecular beam epitaxy. Cube on cube epitaxial growth of Cu_2O thin films on both bulk MgO (0 0 1) and biaxially textured thin films of MgO (0 0 1) was observed and confirmed via X-ray diffraction and reflection high energy electron diffraction measurements. In addition, epitaxial *m*-plane ZnO growth via plasma-assisted MBE was conducted on both MgO substrates and Cu_2O/MgO substrates. The ability to grow oriented, high-quality n-ZnO/p-Cu_2O heterostructures enables improved thin film morphology and may have important implications for optoelectronic and photovoltaic devices.

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1. Introduction

Cuprous oxide (Cu_2O) is a non-toxic semiconductor with a direct band gap of 2.17 eV [1], which is potentially useful for photovoltaic cells and photo-electrolysis of water. It has been reported to have a long minority carrier diffusion length ($\sim$5 μm) [2], and is also composed of both earth-abundant and inexpensive elements [3]. Cuprous oxide is typically a p-type semiconductor due to intrinsic doping by copper vacancies, and efforts to form high-quality homojunctions by n-doping of Cu_2O have largely been unsuccessful. However recent reports include n-type doping of Cu_2O films grown by electrodeposition [4], and homojunctions with reported 200 mV open circuit voltages [5], but the source of n-type doping and voltage remain controversial [6]. Consequently, photovoltaic devices employing Cu_2O are likely to use either the Schottky barriers or the semiconductor heterojunctions as a means for charge carrier separation. The approach taken in this paper anticipates the use of n-ZnO as the heterojunction partner for p-Cu_2O in photovoltaic devices. There have been many reports on Cu_2O solar cells prepared by various techniques, including electrodeposition [3], thermal oxidation of copper sheets [7], and sputter deposition [8]. However, the energy conversion efficiencies of these cells were only a fraction of their respective Shockley–Queisser theoretical values. To date, Cu_2O p–n heterojunctions have not demonstrated good photovoltaic performance, but in most of the previous investigations of Cu_2O thin film growth, film orientation and microstructure were not well controlled. The lack of high-quality heterojunction interfaces between Cu_2O and ZnO reduced the open circuit voltage and fill factor, resulting in a record efficiency of only 2% [9].

In this paper, we investigate the growth of epitaxial MgO, Cu_2O, and ZnO by molecular beam epitaxy in order to better understand and control the heterostructure properties. *In situ* characterization of film structure and orientation was performed using reflection high energy electron diffraction (RHEED). Further post-growth structural analysis was performed via X-ray diffraction $\omega-2\theta$ and rocking curve measurements using Cu K_α radiation.

2. Experimental

Plasma-assisted molecular beam epitaxy (MBE) was used for the fabrication of Cu_2O thin films, as it provided control over critical growth conditions such as temperature, flux, base pressure, and interface sharpness. We used two types of substrates for film growth: cubic single crystal magnesium oxide MgO (0 0 1) and biaxially textured thin films of $MgO/SiO_2/Si$ grown by ion beam-assisted deposition (IBAD) [10]. The IBAD method allows the formation of MgO templates on inexpensive substrates, and could allow the growth of a tandem structure comprised of a Cu_2O thin film cell on top of a solar cell fabricated on a bulk wafer

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substrate (e.g., Si bottom cell). For bulk MgO substrates there is a lattice mismatch of only 1.1% between Cu_2O ($a=0.427$ nm) and MgO ($a=0.422$ nm), which facilitated epitaxial growth. In MBE growth, a copper effusion cell was operated with a beam equivalent pressure of 5×10^{-7} Torr in the presence of a RF oxygen plasma ($P=300$ W) at 10^{-6} Torr , which resulted in a deposition rate of .025 nm/s. MgO substrates were annealed for 1 hour at $T=650$ °C with varying partial pressures of oxygen in the range

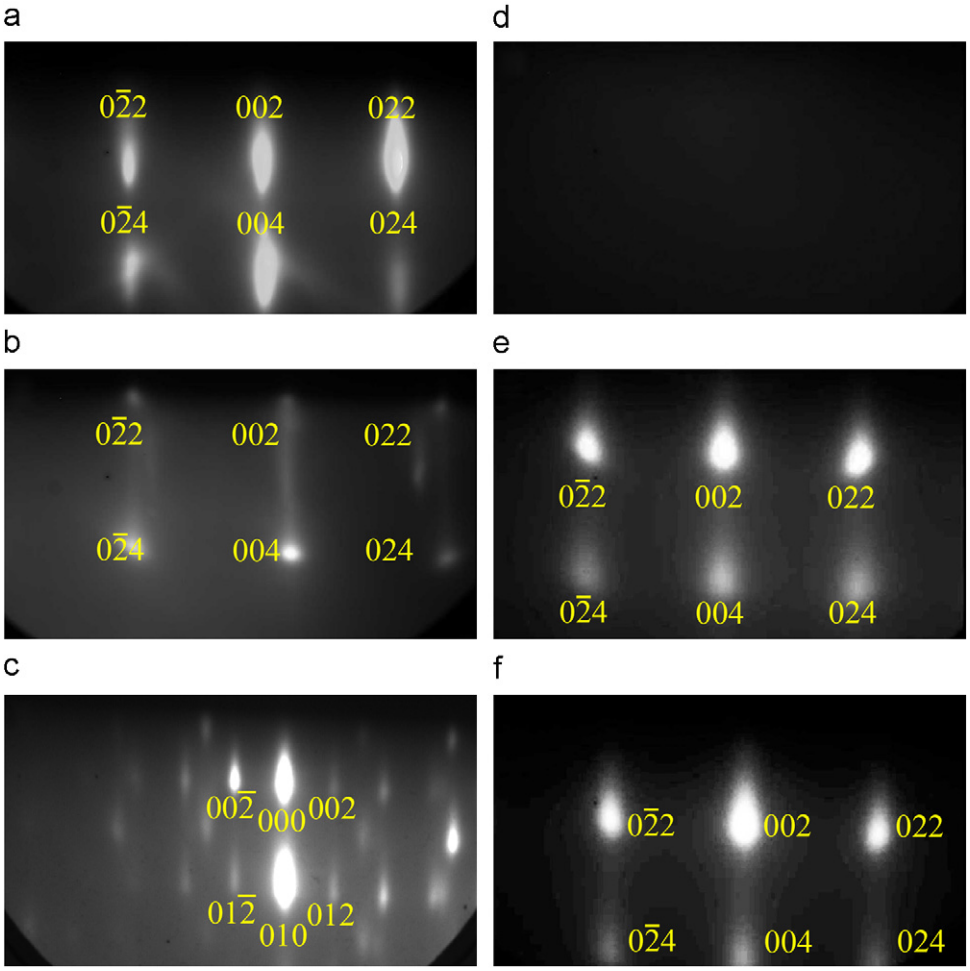

Fig. 1. *In situ* RHEED images from a clean MgO(0 0 1) substrate (a) followed by the deposition of a 70 nm Cu_2O film (b) and 70 nm *m*-plane ZnO on top of the Cu_2O layer are shown on the right hand column. *In situ* RHEED images of a clean SiO_2 surface (d) followed by 10 nm deposition of IBAD MgO(0 0 1) (e) and 70 nm of Cu_2O (f) are shown on the left hand column.

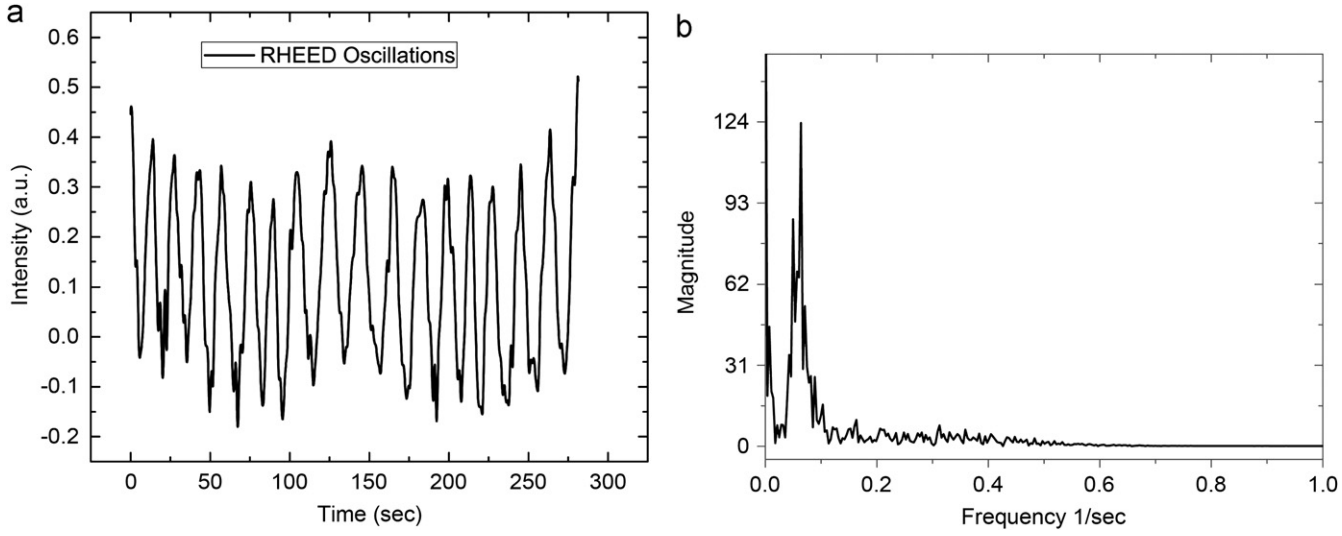

Fig. 2. (a) RHEED oscillations demonstrating layer-by-layer epitaxial growth of Cu_2O on MgO. (b) Fourier transform of RHEED oscillations to determine growth rate.

$P_{O2}=10^{-4}$–10^{-6} Torr, where a pressure $P_{O2}=10^{-6}$ Torr provided the sharpest RHEED patterns.

Ion beam-assisted deposition of biaxially textured MgO (0 0 1) on amorphous SiO_2 was conducted and film orientation was confirmed via RHEED, as illustrated in Fig. 1. IBAD was executed as a three-phase process where a 750 eV Ar^+ ion beam was directed toward an amorphous substrate at a 45° angle for the deposition of MgO by e-beam evaporation. During the first phase, an amorphous MgO film less than 4 nm thickness was deposited. During the second phase of growth, MgO crystals nucleated via solid phase crystallization with out-of-plane texturing. In the third stage of growth, in-plane texturing was evolved due to the amorphization of grains with misaligned in-plane texturing from the Ar^+ ions. The Ar^+ ions channeled in the (0 1 1) direction and

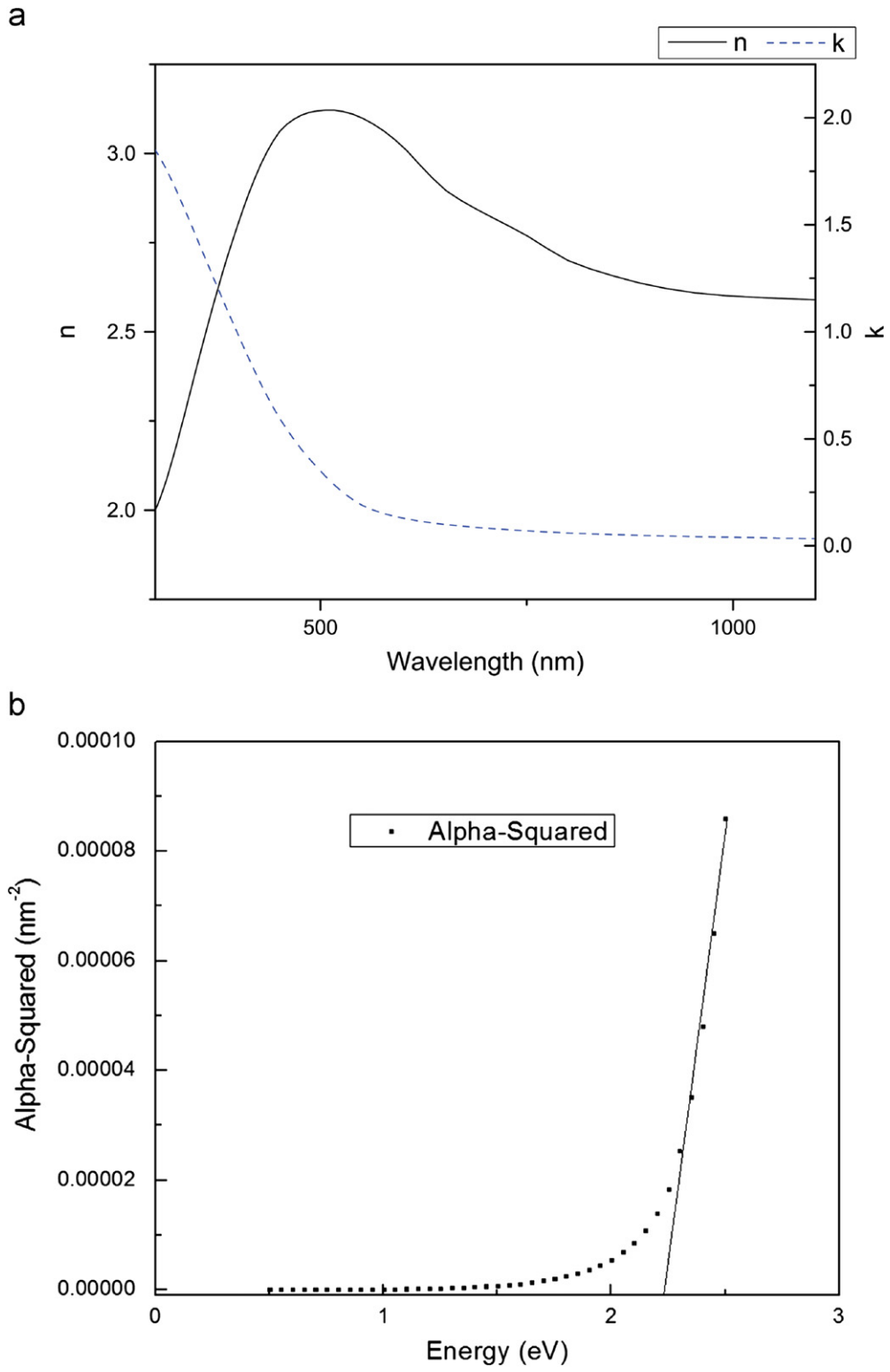

Fig. 3. Spectroscopic ellipsometry data for real and imaginary index of refraction for Cu_2O (70 nm) thin film. Inset shows alpha squared vs. energy, which allows extrapolation of band gap of Cu_2O to approximately 2.2 eV.

amorphized the grains that were not in the (0 0 1) direction. When a sufficiently thick MgO film was deposited, a (0 0 1) MgO film texture was formed as a result of a competitive amorphization process in which Ar^+ ion channeling along [1 1 0] directions minimizes damage for the (0 0 1) film orientation but amorphizes grains with other orientations. This Ar^+ ion beam was then turned off after 10 nm of growth and epitaxial MgO was deposited at an elevated substrate temperature to create a reduced defect density MgO (0 0 1) substrate template. It was then possible to grow Cu_2O with microstructure and properties similar to films grown on bulk MgO substrates.

We used thermally oxidized silicon wafers with a 1 μm amorphous SiO_2 layer as starting substrates for IBAD growth. Using e-beam evaporation, thin films of MgO were deposited at room temperature on our SiO_2 substrates at a rate of 0.2 nm/s with simultaneous ion bombardment by 750 eV Ar^+ ions from a Kaufman source ion gun until the MgO film thickness reached approximately 10 nm. A second electron-beam evaporation step was conducted at an elevated substrate temperature without the ion beam to produce a higher quality MgO film. The surface morphology and its evolution during growth of the biaxially textured MgO films were monitored using RHEED analysis. The second MgO deposition step added approximately 5 nm of MgO for a total MgO thickness of 15 nm in the biaxially textured template substrate.

ZnO thin films were grown (growth rate of 0.2 nm/s) on MgO (0 0 1) substrates and on Cu_2O (0 0 1)/MgO (0 0 1) substrates by MBE using a zinc effusion cell and a RF oxygen plasma. Prior to the ZnO growth, the substrates were thermally cleaned at $T=450$ °C in the presence of the oxygen plasma for 15 min. ZnO was then grown at a substrate temperature $T=350$ °C in the presence of a RF oxygen plasma ($P=200$ W) at 5×10^{-5} Torr with

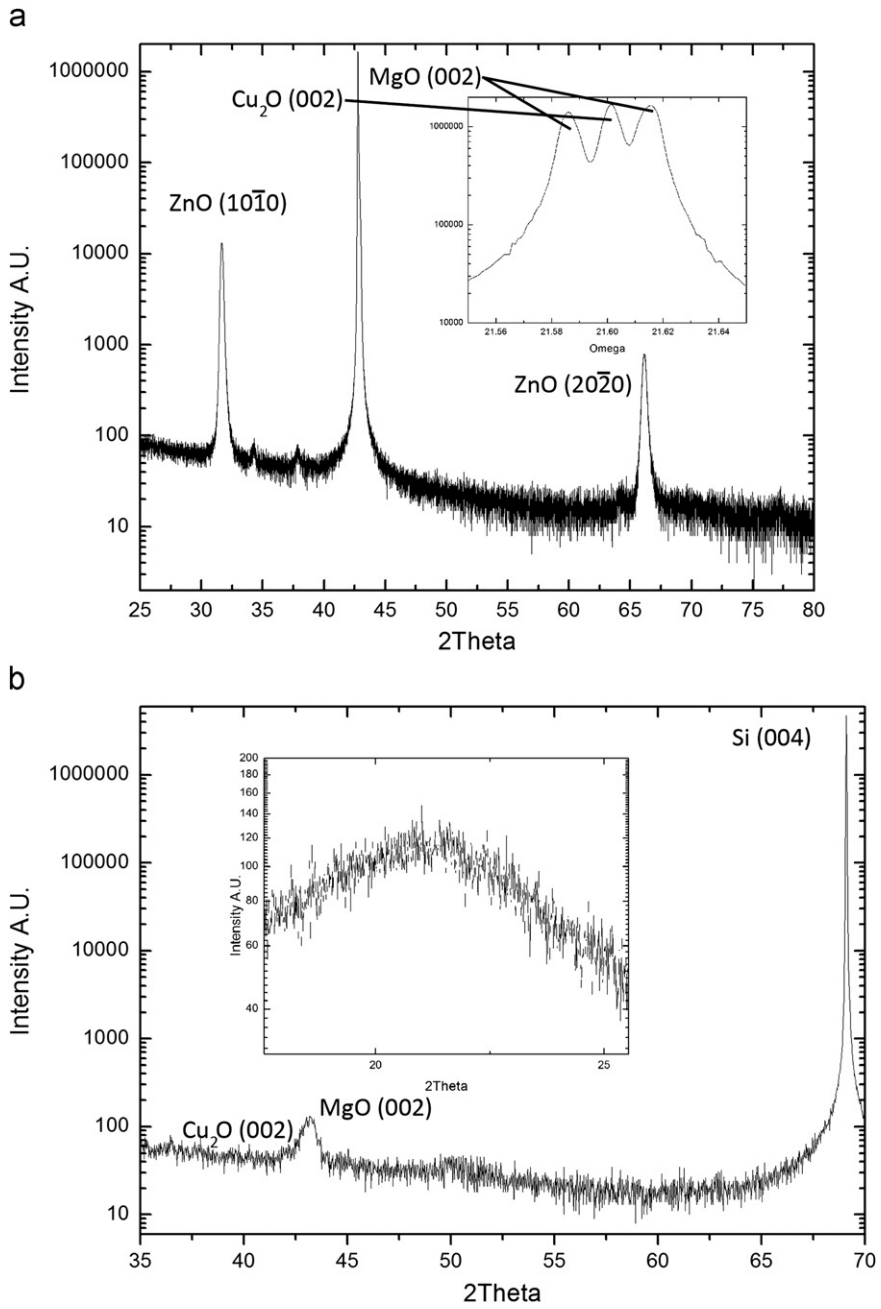

Fig. 4. (a) ω–2θ X-ray scan of (1 0 $\bar{1}$ 0) ZnO (70 nm)/(0 0 2) Cu_2O (70 nm)/(0 0 2) MgO with ω rocking curve of (0 0 2) Cu_2O on (0 0 2) MgO peak. (b) ω–2θ X-ray scan of (0 0 2) Cu_2O (70 nm) on (0 0 2) IBAD MgO (10 nm) grown on an oxidized silicon substrate with ω rocking curve of (0 0 2) Cu_2O on (0 0 2) MgO peak.

a Zn beam equivalent pressure of 10^{-6} Torr. The growth rate of 0.2 nm/s was critical in obtaining the *m*-plane (1 0 $\bar{1}$ 0) orientation of ZnO as opposed to the typically observed *c*-plane (0 0 0 1) orientation.

3. Results and discussion

Both the MgO substrate and Cu_2O film exhibited a cubic crystal structure and closely matched lattice parameters. Cube on cube epitaxy of Cu_2O (0 0 1) was observed on MgO (0 0 1) (T_{sub}=650 °C, RF oxygen plasma (P=300 W) at 10^{-6} Torr, Cu BEP 5×10^{-7} Torr), and *in situ* RHEED was used to confirm the epitaxial growth, as illustrated in Fig. 1. The thickness of the layers was 70 nm for both the Cu_2O and ZnO. The observed RHEED oscillations, shown in Fig. 2, indicated layer-by-layer growth of the Cu_2O film in a two-dimensional island nucleation regime. For Cu_2O (0 0 1)/MgO (0 0 1) epitaxy was observed in the temperature range of T_{sub}=550–650 °C, and RHEED oscillations were typically seen if growth of the film could be well controlled and grown slowly (approximately 0.2 Å/s). The streaky nature of the RHEED images indicated that the Cu_2O films were relatively smooth. The surface roughness of the film slightly increased as a function of the film thickness, evident by the fading intensity of the RHEED pattern. A one-hour anneal at T_{sub}=650 °C and $P_{O2}=10^{-6}$ Torr restored a great deal of the intensity and decreased the surface roughness. X-ray diffraction data illustrated in Fig. 4 confirmed the (0 0 1) Cu_2O orientation and rocking curve analysis showed epitaxial growth of Cu_2O on MgO with (0 0 1) peaks at ω=21.58° and 21.61° for Cu_2O and MgO, respectively.

In addition to structural properties, the electronic and optical properties of Cu_2O films were also characterized. Hall measurements showed hole mobilities in the range of 50–70 cm^2/V s and hole concentrations in the range of $10^{16}/cm^3$, which is dependent on substrate temperature history and oxygen plasma partial pressure during Cu_2O film growth and cool-down. Spectroscopic ellipsometry was performed at an angle of incidence of 50°, 60°, and 70° for $300<\lambda<850$ nm with a Xe lamp visible light source. The $\psi(\omega)$,$\Delta(\omega)$ data were converted to the $n(\omega)$,$k(\omega)$ values in Fig. 3(a), assuming bulk-like isotropic Cu_2O films on MgO (0 0 1) substrates. Using the ellipsometry measurements, we were also able to extrapolate the energy band gap of the Cu_2O film to 2.2 eV, shown in Fig. 3(b), which agrees with previously reported studies [8].

MgO substrates were also used for the growth of ZnO by oxygen plasma-assisted MBE. On nucleation of the film, the RHEED patterns illustrated in Fig. 1 transitioned from a streaky to a spotty pattern, indicating a single predominant orientation of growth. The crystalline orientations as determined by analysis of both the RHEED pattern (Fig. 1) and XRD (Fig. 4) showed a preferential orientation of ZnO in the (1 0 $\bar{1}$ 0) direction. The (1 0 $\bar{1}$ 0) peak corresponds to the *m*-plane of ZnO. Similar results were obtained when growing ZnO on Cu_2O thin films that were grown on MgO.

4. Conclusion

We have achieved epitaxial growth of Cu_2O and ZnO on both single crystal (0 0 1) MgO and (0 0 1) IBAD MgO substrates. MBE growth of the Cu_2O/ZnO heterojunction enabled a high degree of control over crystal orientation and interface quality. Structural, optical, and electrical qualities of the film were characterized using RHEED, X-ray diffraction, spectroscopic ellipsometry, and Hall measurements. These measurements confirmed the high morphological and electrical quality of epitaxially grown Cu_2O films. We have also successfully demonstrated MBE growth of epitaxial ZnO on (1 0 $\bar{1}$ 0) bulk MgO (0 0 1) and on Cu_2O (0 0 1) films.

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References

[1] T. Minami, T. Miyata, K. Ihara, Y. Minamino, S. Tsukada, Effect of ZnO film deposition methods on the photovoltaic properties of ZnO–Cu_2O heterojunction devices, Thin Solid Films (2006) 47–52.
[2] C.A. Dimitriadis, L. Papadimitriou, N.A. Economou, Resistivity dependence of minority carrier diffusion length in single crystals of Cu_2O, J. Mater. Sci. Lett. (1983) 691–693.
[3] S. Ishizuka, K. Suzuki, Y. Okamoto, M. Yanagita, T. Sakurai, K. Akimoto, N. Fujiwara, H. Kobayashi, K. Matsubara, S. Niki, Polycrystalline n-ZnO/p-Cu_2O heterojunctions grown by RF-magnetron sputtering, Phys. Status Solidi (1996) 399.
[4] K. Han, M. Tao, Electrochemically deposited p–n homojunctions cuprous oxide solar cells, Sol. Energy Mater. Sol. Cells (2009) 153–157.
[5] D. Scanlon, G. Watson, Undoped n-Type Cu_2O: Fact or Fiction?, J. Phys. Chem. Lett. (2010) 2582–2585.
[6] C. McShane, Effect of Junction morphology on the performance of polycrystalline Cu_2O homojunction solar cells, J. Phys. Chem. Lett. (2010) 2666–2670.
[7] J. Katayama, K. Ito, M. Matsuoka, J. Tamaki, Performance of Cu_2O/ZnO solar cell prepared by two-step electrodeposition, J. Appl. Electrochem. (2004) 687.
[8] N. Naka, K. Ito, M. Matsuoka, J. Tamaki, Thin films of single-crystal cuprous oxide grown from the melt, Jpn. J. Appl. Phys. (2005) 5096.
[9] A. Mittiga, E. Salza, F. Sarto, M. Tucci, R. Vasanthi, Heterojunction solar cell with 2% efficiency based on a Cu_2O substrate, Appl. Phys. Lett (2006) 163502.
[10] R. Brewer, H.A. Atwater, Rapid biaxial texture development during nucleation of MgO thin films during ion beam-assisted deposition, Appl. Phys. Lett (2002) 3338.