Applied Surface Science 258 (2012) 9949–9953

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

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

Morphological study of PLD grown CuO films on $SrTiO_3$, sapphire, quartz and MgO substrates

M. Kawwam[a,b,*], F. Alharbi[c,d], A. Aldwayyan[b,f], K. Lebbou[a]

[a] Laboratoire de Physico Chimie des Matériaux Luminescents (LPCML), UMR 5620, CNRS Université de Lyon 1, 69622 Villeurbanne cedex, Lyon, France
[b] King Abdullah Institute for Nanotechnology, Riyadh, Saudi Arabia
[c] Energy Research Institute, King Abdulaziz City for Science and Technology (KACST), Riyadh, Saudi Arabia
[d] Qatar Environment & Energy research institute, Doha, Qatar
[f] Department of Physics and Astronomy, King Saud University, Riyadh, Saudi Arabia

ARTICLE INFO

Article history:
Received 5 April 2012
Received in revised form 22 April 2012
Accepted 15 June 2012
Available online 23 June 2012

Keywords:
Thin film morphology
CuO
Pulsed laser deposition
Surface roughness

ABSTRACT

Cupric oxide (CuO) films were prepared on various substrates by the pulsed laser deposition (PLD) technique to investigate their effects on surface morphology. As the substrate temperature decreased, the film surface roughness was also observed to decrease. This trend was also correlated with the polycrystalline structure of the films. Deposition at low pressures produced greater surface roughness because larger crystallites emerged from the surface, while higher oxygen pressure under an adjusted target–substrate distance produced smaller crystallites and a smoother film surface. Reducing the laser energy density led to lower densities and smaller micro-liquid droplets formed on the surfaces. The presented results could be useful for better understanding the effect of process parameters control on CuO film morphology. It could also serve as a reference for the fabrication of CuO-based devices, in which the surface quality of the CuO films is highly important.

1. Introduction

Because of their optical and electrical properties (1.2–1.5 eV band gap) [1–5], CuO have attracted interest as promising materials for solar cells. In practice, solar cells require proper layering of very-high-quality thin films with optimised surface morphology and crystallinity to prevent the surface roughness from affecting carrier transport in the cells. Such growth is not trivial for CuO because different phases of copper oxide are structurally possible and stable, and CuO has a complex monoclinic crystallographic structure ($a = 0.4684$ nm, $b = 0.3425$ nm, $c = 0.5129$ nm, $\beta = 99.471$) [14]. The structural analysis and characterisation of the physical properties of CuO thin films grown by various techniques have been widely reported. The most important deposition techniques used are sputtering [5,6], thermal evaporation and oxidation [2,7,8], molecular beam epitaxy [9,10], and electrochemical deposition [11,12]. Although PLD is widely used for the growth of oxide films because of its advantage in the stoichiometry conservation of complex materials, only few studies have grown cupric oxides by this technique. The PLD of CuO can yield films with improved qualities; however, there is no straightforward theoretical or experimental model for the deposition processes or the resulting film properties. Hence, optimising the surface film quality, investigating the governing parameters, and understanding the causal mechanisms are of great importance.

In this work, a study of CuO film morphology as a function of PLD parameters is presented. Such process parameters are substrate temperature, background pressure, substrate–target distance, and laser energy density. By proper tuning of these parameters, the film quality can be optimised by controlling the surface kinetics, the PLD plume dynamics, and the splashing effect. The X-ray diffraction (XRD) results show that the deposited films are crystalline. The morphologies of the deposited films were characterised by scanning electron microscope (SEM) and atomic force microscope (AFM).

2. Experimental procedure

Five different sets of CuO films were grown by PLD. The first set was grown on four different epi-polished substrates, $SrTiO_3$ (1 0 0), MgO (1 0 0), sapphire (0 0 0 1) and quartz (0 0 0 1) at an oxygen background pressure of 20×10^{-3} Pa, a substrate temperature of 833 K and a laser energy density of 3 J/cm^2. To identify the best matching substrate, a standard 2-theta XRD scan was performed to study the film crystallinity, and SEM images were taken to investigate the surface morphology. MgO (1 0 0) was selected over the other

* Corresponding author at: Laboratoire de Physico Chimie des Matériaux Luminescents (LPCML), UMR 5620, CNRS Université de Lyon 1, 69622 Villeurbanne cedex, Lyon, France.
E-mail address: Mohammad.kawwam@univ-lyon1.fr (M. Kawwam).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.06.055

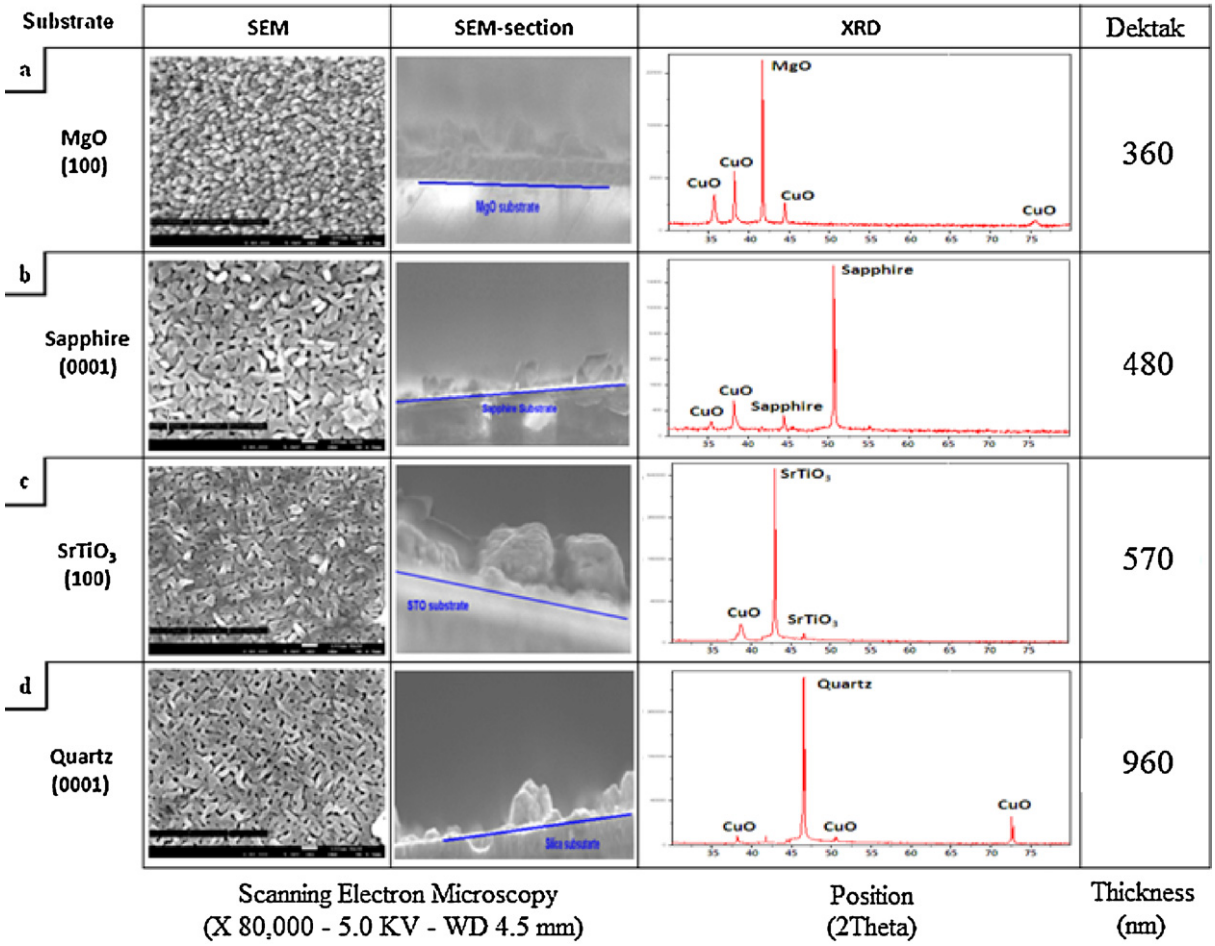

Fig. 1. SEM images, typical XRD (θ–2θ) scans and thickness measurements for PLD grown CuO films, as a function of selected substrate: (a) MgO (1 0 0), (b) Sapphire (0 0 0 1), (c) $SrTiO_3$ (1 0 0) and (d) quartz (0 0 0 1).

substrates for the rest of the work, for reasons that will be discussed later.

The second set of samples was deposited at fixed pressure and laser energy density, and the substrate temperature was varied from 613 to 1013 K. The third set was deposited at fixed temperature and laser energy density, and the gas pressure was varied from 0.5 to 150 $\times$ 10^{-3} Pa. The fourth set was deposited at fixed pressure, temperature and laser energy density, and the target-substrate distance was varied in 2 cm shifts. The last set was deposited at the best obtained temperature, pressure and working distance, but the laser energy densities were varied in 0.25 J/cm^2 shifts.

Before deposition, each substrate was cleaned with acetone and ethanol and dried under nitrogen gas flow. The surface morphology and crystallinity of the substrates were checked by XRD and AFM, respectively, before the substrate was loaded into the PLD chamber. The vacuum chamber was pumped down to 10^{-8} Pa. An *in situ* pre-annealing process was conducted at 1073 K for 45 min under O_2 background pressure for all substrates.

During the deposition, a KrF Excimer laser (COMPex Pro 205, λ = 248 nm, pulse width = 20 ns), which was operated at various energies, was used to ablate a commercial CuO target (99.9% from MTI Corp.). The laser beam was focused on the target at an incidence angle of 45° through a UV-grade quartz window. The ablated species of CuO were ejected with high kinetic energies and deposited on the substrates as they rotated in the off-axis position with respect to the CuO plume normal. During deposition, O_2 gas (99.999% purity) was purged into the chamber through a mass flow controller and a variable leak valve at various pressure ranges. After deposition, the samples were cooled to room temperature at a cooling rate of 5 °C/min. The film thickness profiles were monitored by a Stylus Profiler (Veeco Dektak 150). The surface morphology was imaged by AFM (Veeco multimode V Scan Probe Microscope) and FESEM (JEOL, JSM-7600F). The crystallinity and physical structure were examined by a PANalytical X'Pert X-ray Diffractometer equipped with a Ni filter and using $CuK_{\alpha 1}$ radiation (λ = 1.5405Å).

3. Results

The present study focused on the investigation of the surface morphology of the CuO films to establish the dependence of their surface quality on the growth conditions of the PLD process for further processes optimisation.

3.1. Substrate selection for CuO film growth

The XRD patterns obtained from the CuO films grown on different substrates suggest that the MgO substrate provided the best CuO crystallinity, even for the thinnest film. Fig. 1 shows the evolution of the X-ray diffraction with the choice of substrate, indicating that five peaks attributed to the CuO film were observed in the case of the MgO (1 0 0) substrate. In spite of the higher thickness of the CuO film in the case of the sapphire, $SrTiO_3$ and quartz substrates, the number of peaks and their relative intensities decreased in comparison to those observed on the MgO substrate. In addition, SEM images show that the densest and smoothest film surface morphology was achieved by the film deposited on MgO (Fig. 1). This

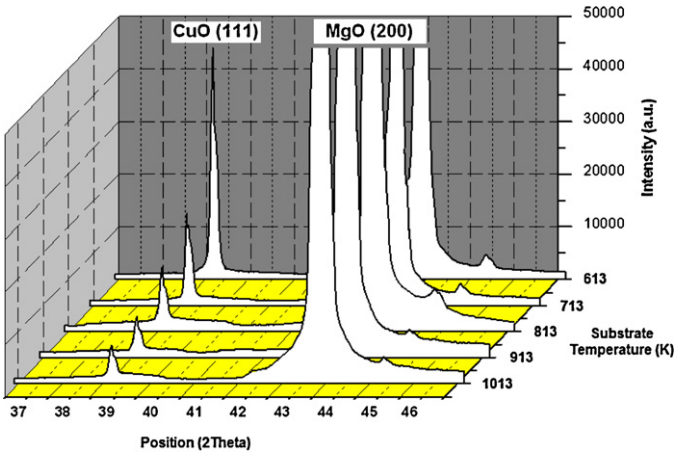

Fig. 2. XRD (θ–2θ) scans for CuO films grown at different MgO substrate temperatures while all other PLD growth parameters being fixed and film thickness was kept around 250 nm for all samples. CuO (1 1 1) peak appears around 38.7°.

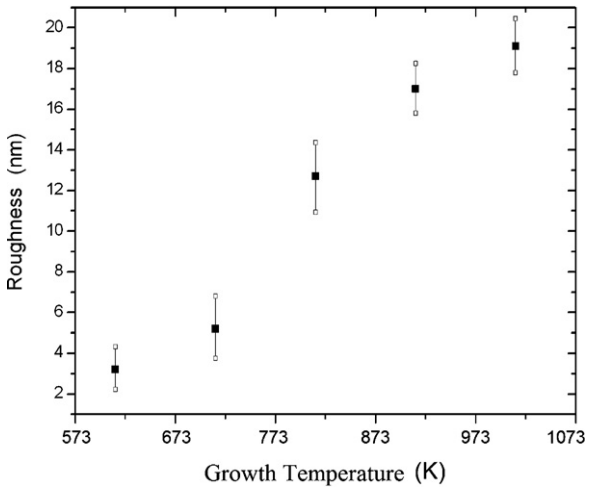

Fig. 3. Surface average roughness (Ra) recorded by AFM for CuO films grown at different substrate temperatures while all other PLD growth parameters being fixed.

result can be explained by the large thermal conductivity of MgO which in comparison to that of the other substrates (1.4, 12, 20 and 30 W/mK for quartz, sapphire, STO and MgO, respectively), providing greater mobility and diffusion effects for species on the surface and affording better nucleation at a given substrate temperature.

The other main factor is the lattice mismatch between the CuO and the substrates. CuO has a monoclinic unit cell with the following dimensions: $a_0 = 4.684$ Å, $b_0 = 3.425$ Å, $c_0 = 5.129$ Å, and $\beta = 99.47°$. In this structure, the Cu atoms stack in chains parallel to [1 1 0] and [−1 1 0], which are separated by oxygen planes. Accordingly, the minimum lattice mismatch occurs in the case of MgO (1 0 0), revealing a probable epitaxial relation for the [1 0 −1] CuO || [1 0 0] MgO orientation, in which the perpendicular spacing corresponds to the distance between the CuO (1 1 1) planes (2.3 Å) [13]. Consequently, MgO was chosen as the substrate for CuO PLD film growth in the remainder of this work.

3.2. Substrate temperature dependence

The film thickness was measured by a Dektak Stylus to maintain a thickness of ~200 nm for all samples. The XRD patterns obtained from the different CuO samples indicate that the film structure consists of a single phase characterised by a double peak at approximately $2\theta = 38.7°$, which is associated with the reflection from the {1 1 1} planes of the CuO crystallites. As shown in Fig. 2, the crystallinity of the CuO films in (1 1 1) direction intensified with decreased temperature. Furthermore, the AFM images of temperature dependence in Fig. 6 indicate that the average surface roughness (Fig. 3) decreased dramatically as the growth temperature decreased.

This improvement occurs because the film species at high temperatures have enough kinetic energy to collide strongly with each other and simultaneously re-evaporate because of the low melting point of CuO compared to the temperature of the PLD plume. Therefore, mass dislocation induces coarseness on the film surface. Additionally, excessively high temperatures produce oxygen vacancies in which interstitial Cu atoms move to the surface, contributing to roughness. In our results, the most crystalline CuO structure with an ideally smooth and dense surface morphology was obtained at a growth temperature of approximately 613 K. This result can be attributed to the actual diffusion length of the species at that temperature, which provides them sufficient time to find energetically favourable lattice positions, reducing the density of surface defects and improving the crystal quality.

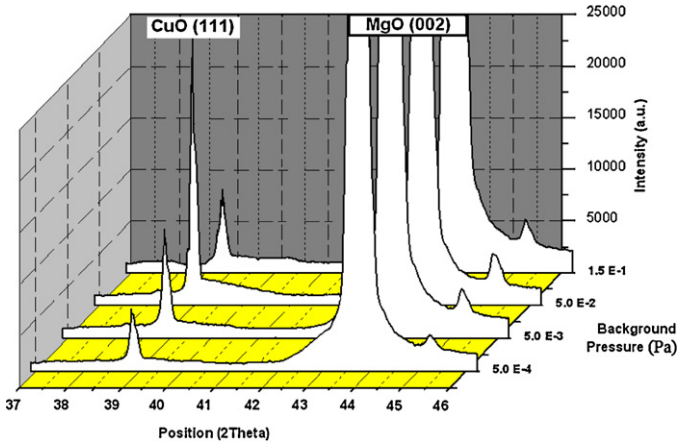

Fig. 4. XRD (θ–2θ) scans for CuO films grown at different O_2 background pressures while all other PLD growth parameters being fixed and film thickness was kept around 250 nm for all samples. CuO (1 1 1) peak appears around 38.7°.

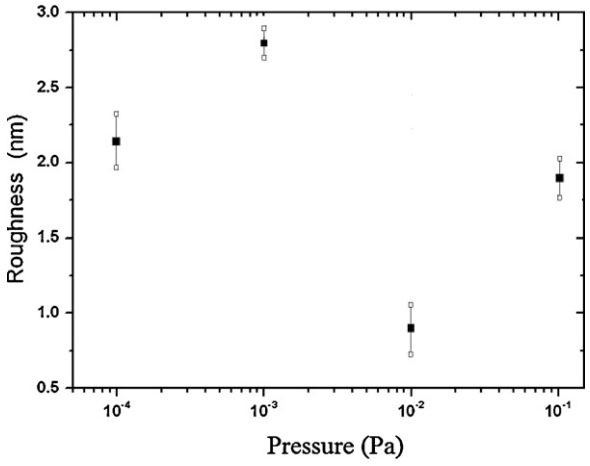

Fig. 5. Surface average roughness (Ra) recorded by AFM for CuO films grown at different O_2 background pressures while all other PLD growth parameters being fixed.

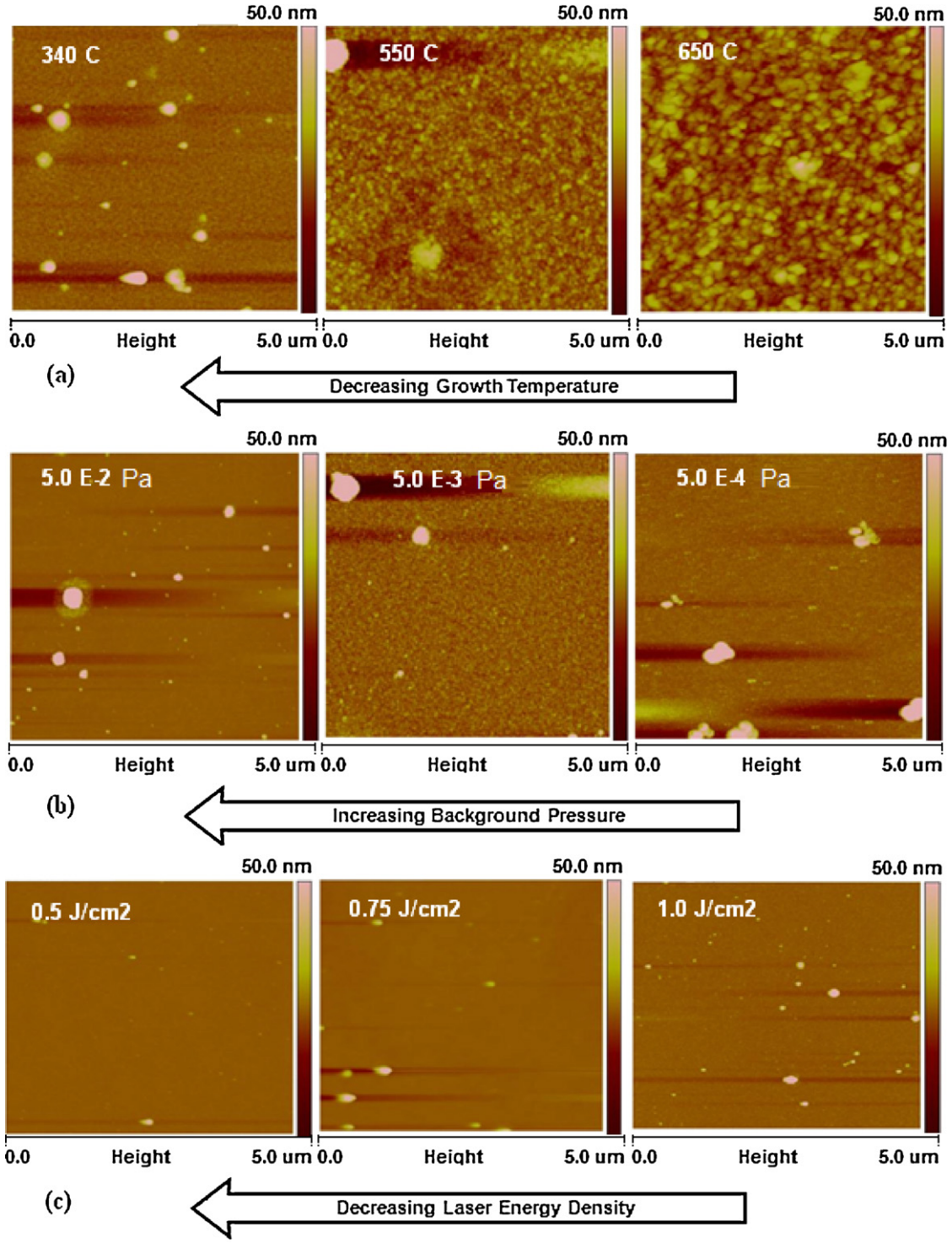

Fig. 6. AFM images for PLD grown CuO films, compared per variation of PLD process conditions: (a) decreasing growth temperature, (b) increasing O_2 background pressure and (c) decreasing laser energy density. All films are grown on MgO (1 0 0).

3.3. Process pressure dependence

In the PLD technique, oxygen gas is often introduced to serve two main purposes. First, the growth of an oxide film requires an oxidising species (typically molecular oxygen) as a background component. In our case, the amount of oxygen to be introduced depended on the thermodynamic stability of the selected copper oxide stable phase, CuO. Increasing the oxygen partial pressure significantly reduced the loss of Cu in the films. The introduction of additional oxygen produced more Cu–O molecules through gas-phase collisions of the disjointed Cu species with oxygen. Increased oxygen partial pressure reduces the probability of desorption of Cu species from the heated substrates and causes the incorporation of more CuO into the films with conserved stoichiometry transfer. Second, in addition to actively participating in the chemistry of oxide growth, the background gas can be used to reduce the kinetic energies of the ablated species. Referring to the XRD results, the strongest intensity of the CuO (1 1 1) peak was found at 50×10^{-3} Pa (Fig. 4) during the growth of samples at varied oxygen pressure. This result indicates the recommended range

of oxygen pressures needed for optimum film chemistry and crystallinity. The amount of surrounding oxygen molecules equivalent to 50×10^{-3} Pa provided optimal oxidation of the ablated materials and moderated their energies before they reached the substrates. Consequently, at lower pressure ranges, the thermal energies of the ablated species could be too high for proper CuO crystalline growth, and the amount of interacting oxygen molecules could be too low for the desired chemistry.

At lower pressure, such as 5×10^{-3} Pa, the film surface acquired a grainy structure (pressure dependence in Fig. 6), implying that its higher thermal energy increased the probability of 3D growth. This result is in agreement with the explanation of the higher growth temperature cases discussed above. However, at the lowest pressure of 0.5×10^{-3} Pa, the film average surface roughness was reduced (Fig. 5). It is possible that the strong PLD plume directly impacted the films as a consequence of the low pressure because there were few gas molecules to stop its elongation towards the substrate. Accordingly, the smoother surface at very low pressure would have been a result of surface etching by the elongated plume. In contrast, when the pressure was increased to 150×10^{-3} Pa, the dynamic energy of the plume was reduced significantly by the denser gas molecule environment. Consequently, the thermal energy was inadequate to form proper CuO crystals, producing a granular surface structure.

3.4. Melt droplets

In the PLD process, a laser beam provides the thermal energy to evaporate the target. If the time required to transform the laser energy to heat energy is shorter than that required to evaporate a subsurface layer with a thickness on the order of the skin depth (optical region), the target is heated to the boiling point, and spherical micro-sized particles (liquid droplets) are ejected from the surface of the target, forming particulates on the film surface. This phenomenon is known as the splashing effect, and it is one potential drawback of PLD because these particles present obvious problems in the formation of multilayer device structures.

Several techniques were developed to reduce the particle density, examples include: velocity filters [15], off-axis laser deposition [16], and line-of-sight shadow masks [17]. In this work, simpler approaches were used and proved to be of significant effect: high-density CuO target, large substrate–target distance, and reduced laser energy density. As a result, the smallest shapes and lowest densities of liquid droplets were observed at the lowest laser energy density (laser fluence dependence in Fig. 6). At the largest working distance (12.5 cm), further surface smoothness was recorded but at a relatively low deposition rate as the kinetic energy of species decreases dramatically as a function of upward distance. To conclude, droplet-free CuO films deposition require low energetic process and large working distances in an ordinary PLD set up.

4. Conclusion

The surface morphologies of the CuO films synthesised by pulsed-laser-deposition under five sets of various process parameters were examined and characterised. From the first set grown on four different substrates, $SrTiO_3$ (1 0 0), MgO (1 0 0), sapphire (0 0 0 1) and quartz (0 0 0 1), MgO (1 0 0) can be selected as the best candidate because it produced better film morphology and crystallinity. The surface roughness exhibited a decreasing trend as the substrate temperature decreased, which also correlates with the polycrystalline structure of the films. The CuO films grown under low pressures had the greatest surface roughness because they had larger crystallites emerging from their surfaces, while the films produced under higher oxygen pressure with target-substrate distance adjustment provided smaller crystallites and smoother film surfaces. As the laser energy density was reduced, the density and size of micro liquid droplets formed on surfaces was also reduced.

In conclusion, MgO (1 0 0) provided the best matching substrate for the growth of CuO {1 1 1} film among the tried substrates. The optimised growth temperature was 613 K, providing the lowest surface roughness and the strongest crystalline peak. An oxygen pressure of 50 mTorr with an adjusted target–substrate distance produced the lowest surface roughness. As the laser energy density decreased to 0.5 J/cm^2, the formation of micro liquid droplets on the CuO film surface was reduced significantly.

The oxygen rf-plasma-assisted PLD technique is under investigation and will be performed to obtain better stoichiometric conservation of the ablated CuO and minimal oxygen deficiencies in the grown films. In this way, it should be possible to grow films with reduced structural stresses and dislocations, providing smoother film surfaces and structures of greater crystallinity. Further work is under way to clarify this process and its effects on the optical and electrical properties of PLD-grown CuO films.

Acknowledgments

This work was supported by King Abdulaziz City for Science and Technology. The authors also thank Dr. Jeonggoo Kim from NEOCERA Inc., USA and Prof. Mahmoud Korek from Beirut Arab University, Lebanon for the fruitful discussions.

References

[1] F. Marabelli, G. Parravicini, F. Salghetti-Drioli, Optical gap of CuO, Physical Review B 52 (1995) 1433–1436.
[2] A. Jayatissa, K. Guo, A. Jayasuriya, Fabrication of cuprous and cupric oxide thin films by heat treatment, Applied Surface Science 255 (2009) 9474–9479.
[3] X. Rocquefelte, M. Whangbo, A. Villesuzanne, S. Jobic, F. Tran, K. Schwarz, P. Blaha, Short-range magnetic order and temperature-dependent properties of cupric oxide, Journal of Physics: Condensed Matter 22 (2010) 045502.
[4] N. Hoa, S. An, N. Dung, N. Van Quy, D. Kim, Synthesis of p-type semiconducting cupric oxide thin films and their application to hydrogen detection, Sensors and Actuators B: Chemical 146 (2010) 239–244.
[5] T. Darma, A. Ogwu, F. Placido, Effects of sputtering pressure on properties of copper oxide thin films prepared by rf magnetron sputtering, Materials Technology: Advanced Performance Materials 26 (2011) 28–31.
[6] H. Lu, C. Chu, C. Lai, Y. Wang, Property variations of direct-current reactive magnetron sputtered copper oxide thin films deposited at different oxygen partial pressures, Thin Solid Films 517 (2009) 4408–4412.
[7] F. Li, R. Waddingham, W. Milne, A. Flewitt, S. Speakman, J. Dutson, S. Wakeham, M. Thwaites, Low temperature (100 °C) deposited P-type cuprous oxide thin films: importance of controlled oxygen and deposition energy, Thin Solid Films (2011), http://dx.doi.org/10.1016/j.tsf.2011.04.192.
[8] G. Papadimitropoulos, N. Vourdas, V. Vamvakas, D. Davazoglou, Optical and structural properties of copper oxide thin films grown by oxidation of metal layers, Thin Solid Films 515 (2006) 2428–2432.
[9] R. Kita, K. Kawaguchi, T. Hase, T. Koga, R. Itti, T. Morishita, Effects of oxygen ion energy on the growth of CuO films by molecular beam epitaxy using mass-separated low-energy O+ beams, Journal of Materials Research 9 (1994) 1280–1283.
[10] K. Muthe, J. Vyas, S. Narang, D. Aswal, S. Gupta, D. Bhattacharya, R. Pinto, G. Kothiyal, S. Sabharwal, A study of the CuO phase formation during thin film deposition by molecular beam epitaxy, Thin Solid Films 324 (1998) 37–43.
[11] A. Yin, J. Li, W. Jian, A. Bennett, J. Xu, Fabrication of highly ordered metallic nanowire arrays by electrodeposition, Applied Physics Letters 79 (2001) 1039.
[12] E. Morrison, D. Gutiérrez-Tauste, C. Domingo, E. Vigil, J. Ayllón, One step room temperature photodeposition of Cu/TiO_2 composite films and its conversion to CuO/TiO_2, Thin Solid Films 517 (2009) 5621–5624.
[13] A. Catana, J. Locquet, S. Paik, I. Schuller, Local epitaxial growth of CuO films on MgO, Physical Review B 46 (1992) 15477.
[14] J.B. Forsyth, S. Hull, The effect of hydrostatic pressure on the ambient temperature structure of CuO, Journal of Physics: Condensed Matter 3 (1991) 5257–5261.
[15] E.V. Pechen, A.V. Varlashkin, S.I. Krasnosvobodtsev, B. Brunner, K.F. Renk, Applied Physics Letters 66 (1995).
[16] B. Holzapfel, B. Roas, L. Schultz, P. Bauer, G. Saemann-Ischenko, Applied Physics Letters 61 (1992) 3178–3180.
[17] Z. Trajanovic, S. Choopun, R.P. Sharma, T. Venkatesan, Applied Physics Letters 70 (1997) 3461–3463.