Chapter 3 Structure, Morphology and Defect analysis of low temperature grown Copper oxides

The objective of this work is to synthesise high quality, phase pure cuprous oxide as light absorber materials both for sustainable metal oxide based thin films solar cells and photo electrochemical cells for water splitting, especially for H_2 evolution. In past years, several physical and wet-chemical based deposition methods have been employed to produce high optoelectronic quality single phase copper oxides, but in most cases the resulted films are of either low electronic quality, for example highly resistive electrodeposited thin films or mixed phase copper oxide compounds in case of high vacuum system based techniques. In case of vacuum system based technique, PLD, CVD and RF-Magnetron sputtering have been extensively used to optimize physical, structural and optoelectronic properties with varying process conditions, but with less success in fabricating solar cells. The PLD technique for growing copper oxide has been explored less and only a handful of works have been done but at high process temperatures (>650 ^{0}C). In this Chapter, we explored the formation of copper oxide thin films onto a variety of substrates by varying growth conditions and post-deposition analysis to give insights into the factors that influence the film growth kinetics, structural properties, composition, and morphology. The influence of growth conditions is divided into three parts: ***Part I Effect of substrate temperature****,* ***Part II Influence of oxygen partial pressure****, and* ***Part III Effect of laser fluence and substrate type****.*

3.1 Introduction

Cuprous oxide(Cu_2O), a naturally stoichiometric defect type semiconductor, has been showing much promise in photo catalytic water splitting, gas sensor, as a negative electrode in Li-ion based batteries [1-4] and more extensively in photovoltaic (PV) technology in recent years because of its environmentally benign nature, optimal band gap for harnessing sunlight, low cost due to material abundance in the earth crust and ease of the fabrication process[2, 5-7]. In past years, several physical and wet-chemical based deposition methods have been tried to produce high quality phase pure Cu_2O, among them thermal oxidation [7-9], electrodeposition [2, 10-13] and magnetron-sputtering [3, 5, 14] are the most popular growth techniques. Thermal oxidation potentially produces highly crystalline, reasonably good electronic quality as well as single phase Cu_2O[9] material but its high process temperature limits applications. Moreover, high-temperature grown Cu_2O films were reported to contain "voids, inclusion and low-angle grain boundaries" which substantially contribute to the low device performance despite of their single crystal form[7]. On the other hand,

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3.3.3.5 Surface morphology

The surface morphology of PLD grown films were conducted by using both scanning electron microscope (JEOL 6330 FEG-SEM) in secondary electron(SE) image mode and atomic force microscope(AFM-Vecco 3D NanoScope) in tapping mode. The energy dispersive X-ray(EDX) detector, coupled with the field emission gun scanning electron microscope(FEG-SEM), was also used for identifying bare substrate and thin film(where necessary).

The variations of oxygen content in the Cu-O-Cu chains are not only directly coupled to the doping level of Cu_2O films but also have unique influence to microstructural changes. In the previous section we observed that O_{2pp} level during PLD negatively affect the grain growth of Cu_2O evident from TEM and XRD results. These observations were further assessed by investigating the surface morphology of films grown with identical[26] deposition conditions.

3.3.3.5.1 Room temperature grown copper oxide thin films

Figure 3.28(overleaf) shows the typical microstructure of the films deposited onto ITO coated glass substrates at 25 °C as a function of O_{2pp}. The morphology of these thin films are found to be initially very rough and the surface are covered by spherical shaped grains (~50nm) while grown with $O_{2pp} \approx$ 2mTorr (figure 3.28(a)) then gradually changed to 2D islands of tiny homogenous grains with decreasing size but introducing more holes and micro-cracks in the film surface while O_{2pp} increased up to 10mTorr in the PLD chamber (figure 3.28 (b – d)).

[26] Different substrates were placed side by side inside the PLD chamber as described in section 3.3

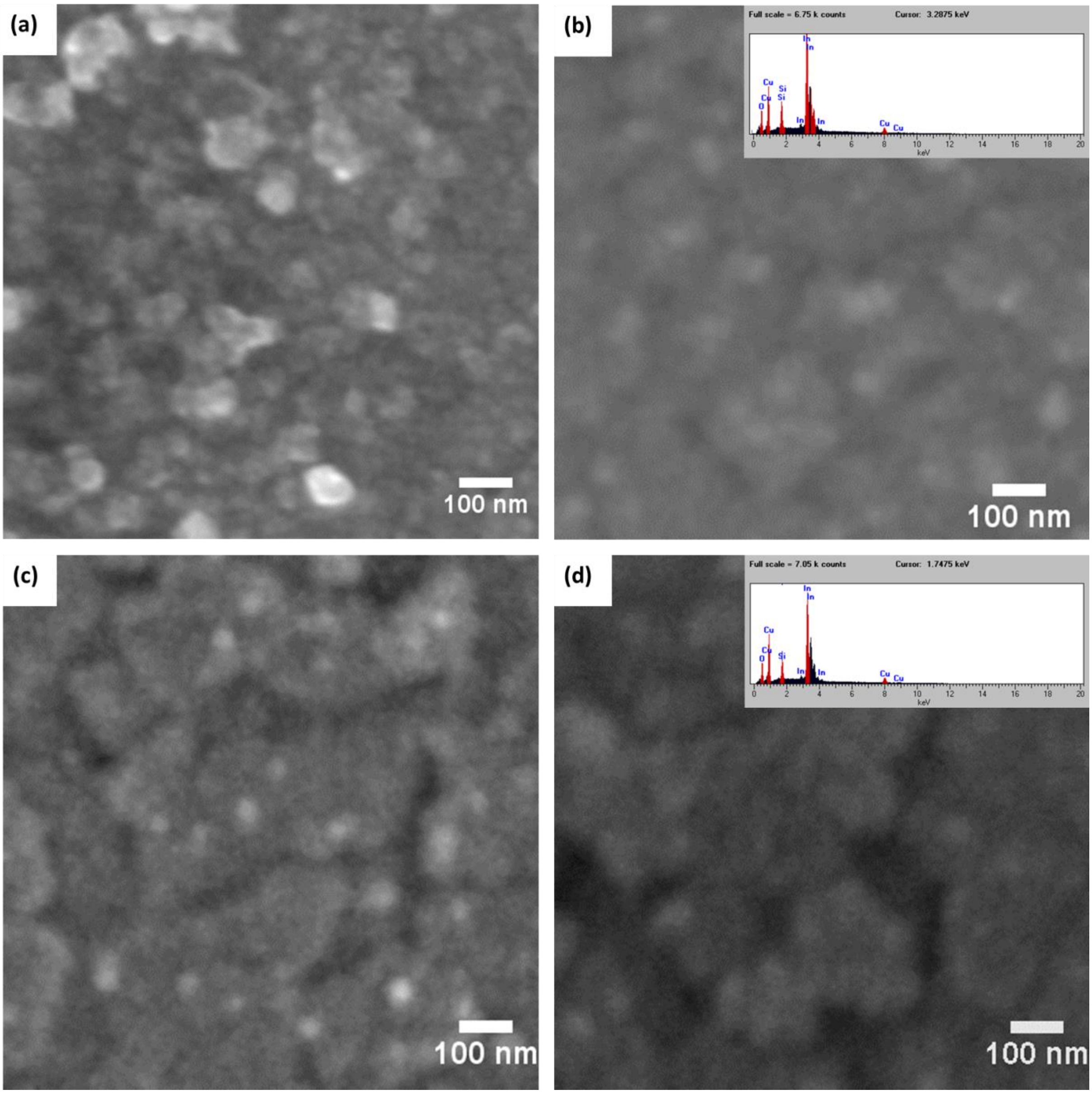

Figure 3.28: SEM micrograph(plane view) of as grown Cu_2O layers at $T_{sub} \approx 25\ ^oC$ with (a) 2 mTorr O_{2pp} , (b) 3 mTorr O_{2pp} , (c) 5 mTorr O_{2pp} , and (d) 10 mTorr O_{2pp} respectively onto ITO coated soda lime glass; the inset shows the EDX spectrum of the respective sample.

Presumably, the RT-grown copper oxide films deposited with 3mTorr $\geq O_{2pp} \geq$ 10mTorr were found to be following the surface morphology of the underlying substrate. Initially it was hard to distinguish from bare ITO substrate (cf. figure 3.30 in next page) but the subsequent EDX analysis confirmed the presence of Cu_2O films (see inset of 3.28(b, d)). Furthermore, tapping mode-AFM images of the same samples revealed that the grains for Cu_2O decreased from ~72 nm to ~44 nm with increasing O_{2pp} from 2mTorr to 10mTorr in the PLD chamber (see figure 3.29). The SEM and AFM images of bare ITO are also shown in figure 3.30 for comparison.

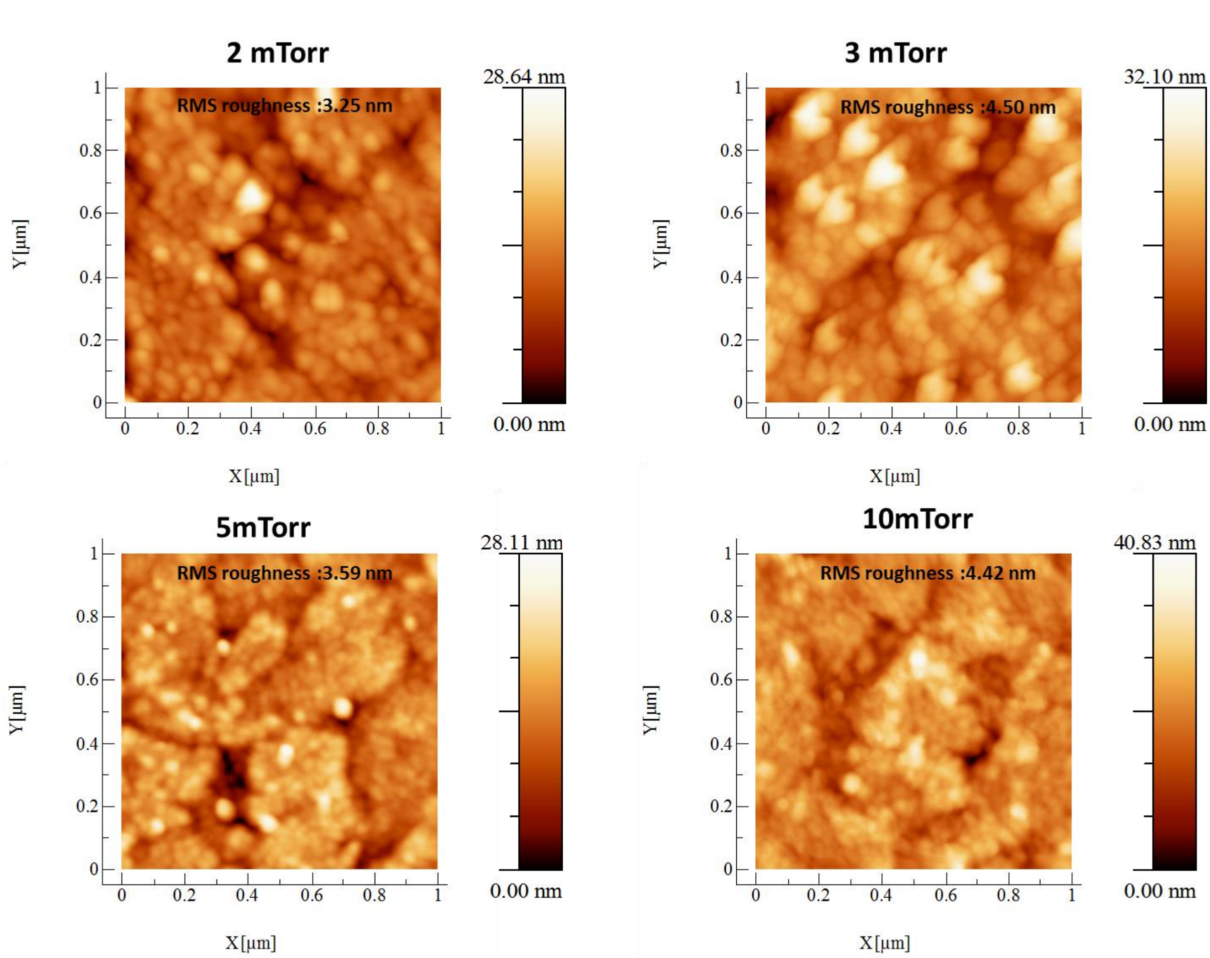

Figure 3.29 AFM micrograph of RT-grown copper oxide layers on ITO coated glass as a function of O_{2pp}. The root mean square (RMS) roughness values are also indicated in the respective image.

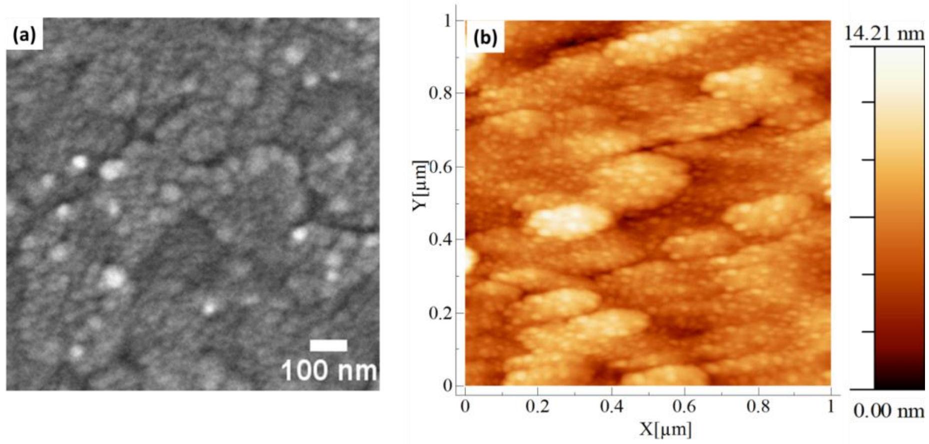

Figure 3.30 Surface morphology of ITO coated glass substrate (Blank) that was used to deposit copper oxide; (a) SEM and (d) AFM (RMS roughness~2.54nm) image.

As can be seen from both SEM and AFM micrographs, the grain size and surface roughness of PLD Cu_2O films are substantially different from the bare ITO substrate; and a reasonably uniform coverage of underlying substrate by copper oxide films is also evident (cf. figure 3.28 – 3.30). Clearly, the trend of decreasing grain size with increasing O_{2pp} is also evident here; and the likely reason could be attributed to two folds: firstly, reduced overall energy of the impinging ablated species available for crystal growth, and secondly, Cu_xO_y(e.g., Cu_3O_2 and/or CuO atop the Cu_2O grains[48]) related phase inclusion in higher O_{2pp} ambient, which is in good agreement with the results described in the section 3.3.2.2.1 and 3.3.3.2. Therefore, the variation of O_{2pp} in PLD films are seen to have remarkable influence in controlling surface morphology which should play important role in controlling electrical conductivity, including phase purity, of copper oxides.

3.3.3.5.2 High temperature grown copper oxide films

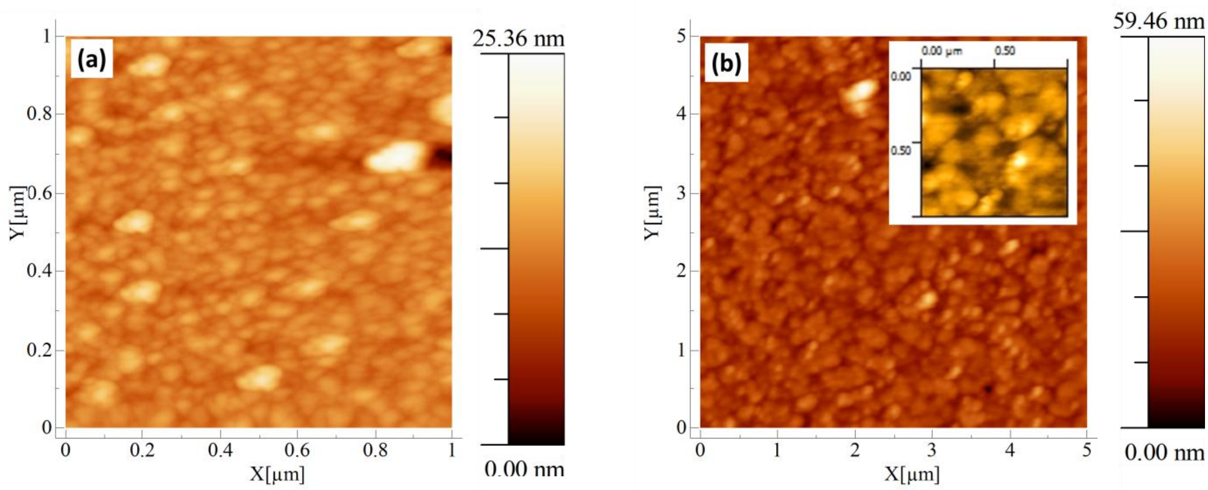

Figure 3.31 Typical AFM micrographs of HT-grown copper oxide layer deposited with O_{2pp} ≈ 7mTorr O_{2pp} onto (a) Quartz glass and (b) ITO coated glass substrate. The inset in (b) shows a magnified area(1 μm × 1 μm).

Figure 3.31 (a) and 3.31(b) show AFM micrographs of HT-grown copper oxide layer deposited with O_{2pp} ≈ 7mTorr O_{2pp} onto Quartz and ITO coated glass substrate, respectively. Despite the incomparable investigated area in AFM, there is a discernible influence in microstructure of HT-grown copper oxide films while grown onto different types of substrates. The films grown onto non-conducting quartz substrate exhibit shiny smoothed surface with RMS roughness~1.86±0.20 nm, while those grown onto conducting ITO substrates exhibit remarkably large grains and abrupt surface with RMS roughness~4.02±0.10 nm (cf. figure 3.31(a) and 3.31(b, inset)). The substrates effects are visibly more pronounced in SEM micrographs of the copper oxide films grown with same processing conditions shown in figure 3.32.

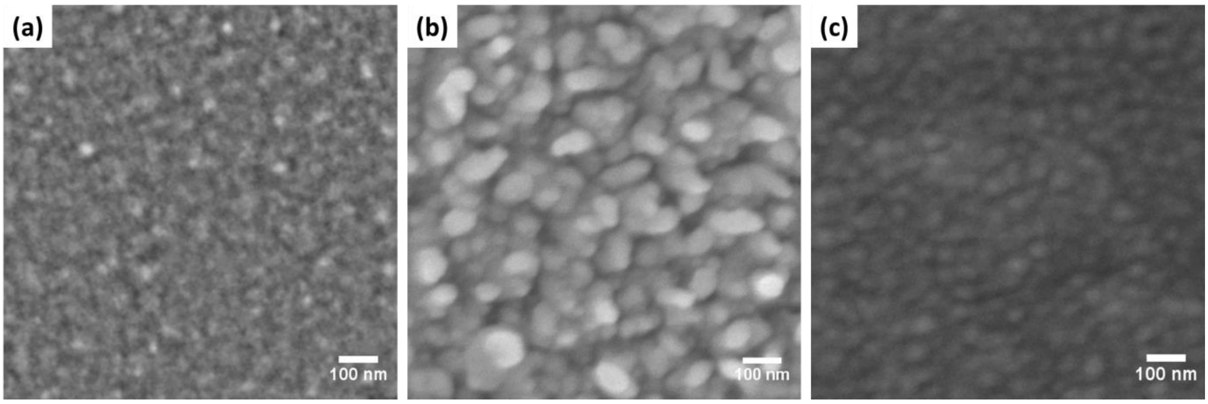

Figure 3.32: SEM micrograph of Cu_2O at $T_{sub}\approx$ 200 ^oC with 7mTorr O_{2pp} onto (a) Quartz glass, (b) FTO coated glass, and (c) Gold coated glass

Clearly, in figure 3.32, the microstructure of HT-grown film onto non-conducting quartz substrate displays distinctive grain features with significantly smaller in size compare to those grown onto conducting FTO and Gold substrates. Furthermore, copper oxide grains in FTO are bean like (dia~150nm) and bigger than those spherical shaped grains(~50nm) appearing in gold substrate, the latter is visibly more compact and pinhole free in 'copper oxide coverage' than the former due to the fact that higher surface mobility of adatoms are expected on gold than on the FTO substrate.

In light of above SEM and AFM observations, HT-grown films are more homogenous in grain size ,conformally coated the underlying substrate, and free from any particulates, micro-cracks, and pinholes in a reasonably large investigated area than those grown at room temperature. This could be attributed as the diffusion of the laser ablated species across the substrate occurs laterally at more ease at elevated temperature. The high substrate temperature allows adatoms/clusters to minimize voids etc. and to follow the morphology of underlying substrate resulting in a uniform coverage. Therefore, the type and nature of substrates surface, including the variation of processing conditions (i.e., O_{2pp} and T_{sub}), has marked effect in determining the microstructure of copper oxide thereby might dictate the electrical properties of the resulting thin films.

3.3.3.6 Conclusions (Part II)

Phase pure Cu_2O thin films were synthesised by PLD over a wide range of growth pressure at two different substrate temperatures, namely $T_{sub} \approx 25\ ^0C$(RT) and $T_{sub} \approx 200\ ^0C$(HT), which are far below the temperature required by the thermodynamic equilibrium (~600 ^0C) within the range of investigated growth pressure cited in the literature[15, 19, 26]. The effect of O_{2pp} in controlling phase composition, microstructure and surface morphology of Cu_2O PLD films were analysed by XRD, TEM, Raman spectroscopy, SEM, and AFM; and the observations are summarized as follows:

(a) Single phase Cu_2O film with varying properties can be achieved in the range 1mTorr $\leq O_{2pp} \leq$ 7mTorr in the case of RT-grown films and 3mTorr $\leq O_{2pp} \leq$ 5mTorr in the case of HT-grown films, the former shows (200) textured films while the later shows (111) textured films as evident from the XRD analyses. Grain size and growth rates are negatively affected with increasing O_{2pp} irrespective of the substrate temperature as evident from both XRD and TEM observations.

(b) RT-grown films were appeared to be more phase-pure than those grown at elevated temperature. The films grown with $O_{2pp} \geq$ 5mTorr contain mixed Cu_xO_y and CuO phase in Cu_2O matrix as evident from XRD and Raman analyses. The SAED pattern of $O_{2pp} \approx$ 5mTorr films turned out to be identical to pure Cu_2O crystal, most probably due to nominal presence of Cu_xO_y phase in the Cu_2O matrix.

(c) Both groups of films were found to be free from CuO and Cu_4O_3 phase within the phase purity limit described in (a), above, as evident from the XRD and Raman analysis.

(d) Surface morphology of RT-grown PLD films as a function of O_{2pp} revealed a trend of decreasing grain size with increasing O_{2pp} as evident both from SEM and AFM analyses which qualitatively corroborated the TEM observations. The HT-grown films were found to be smoother and defect free compared to the RT-grown films. There is a discernible influence of underlying substrate in determining the surface morphology of the resulted PLD films.

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