# Low temperature growth technique for nanocrystalline cuprous oxide thin films using microwave plasma oxidation of copper

K. V. Rajani [a] *, S. Daniels[a], E. McGlynn[b], R. P. Gandhiraman[c], R. Groarke[d] and P. J. McNally[e]

[a]*School of Electronic Engineering and NCPST, Dublin City University, Dublin 9, Ireland*

[b]*School of Physical Sciences and NCPST, Dublin City University, Dublin 9, Ireland*

[c]*BDI, Dublin City University, Dublin 9, Ireland*

[d]*School of Chemical Sciences, Dublin City University, Dublin 9, Ireland*

[e]*School of Electronic Engineering, Dublin City University, Dublin 9, Ireland*

ABSTRACT

We report on the direct formation of phase pure nanocrystalline cuprous oxide ($Cu_2O$) film with band gap ~ 2 eV by microwave plasma oxidation of pulsed dc magnetron sputtered Cu films and the highly controlled oxidation of Cu in to $Cu_2O$ and CuO phases by controlling the plasma exposure time. The structural, morphological and optoelectronic properties of the films were investigated. p-type $Cu_2O$ film with a grain size ~20-30 nm, resistivity of ~66 Ω cm and a hole concentration of $\sim 2\times10^{17}$ $cm^{-3}$ is obtained for a plasma exposure time of 10 min without using any foreign dopants. The optical absorption coefficient (~$10^5$ $cm^{-1}$) of the $Cu_2O$ film is also reported.

Keywords: semiconductors, solar energy materials, oxidation

* Corresponding author. e-mail: kv.rajani2@mail.dcu.ie , Tel: +353 1 700 5872, Fax: +3531700 5508

**1. Introduction**

Cuprous oxide ($Cu_2O$) is a naturally p-type, direct band gap (~2 eV), nontoxic metal oxide semiconductor material possessing a fairly high absorption coefficient in the visible region, with potential applications in solar energy conversion, catalysis and lithium ion batteries [1-2]. In addition, the $Cu_2O$ and CuO nanosystems have great potential for photo-activated hydrogen production, a key solution for the clean and recyclable $H_2$ energy. There are several reports on the growth, characterization and applications of copper

oxides, however, the electrical characteristics of the copper oxide films are strongly influenced by the preparation methods [3]. There are numerous reports on the exploitation of $Cu_2O$ as an active layer for solar cells [4-5]. Even though it has a theoretical conversion efficiency of around 20 %, actual efficiencies reported so far are around 2% [6]. One of the possible reasons for the lower conversion efficiency is the higher series resistance of the fabricated solar cells. Hence the development of $Cu_2O$ material with lower resistivity is very important for the improvement of the power conversion efficiency of solar cells based on this material. Again, uniform nanocrystalline $Cu_2O$ films on appropriate substrates have interesting applications in the field of heterogeneous photocatalysis. Similarly, the applications of CuO in gas sensors and as anodes for organic light emitting diodes and lithium ion batteries are also reported [7-8].

Although $Cu_2O$ has several potential applications, it is difficult to produce phase pure $Cu_2O$ without traces of CuO, which is an impediment for the semiconductor applications of this material. In this letter, we report on the use of a direct and simple processing technique for the low temperature deposition of phase pure $Cu_2O$ with nanocrystalline grains using microwave plasma oxidation of Cu films at 300°C. The microwave plasma can provide an extremely high density of predominantly $O^-$ ions compared to the normal glow discharge. These ions can be implanted into the growing oxide films and cause high oxidation rate of the films [9]. The bombardment of energetic oxygen ions from the plasma produces a quick and uniform oxidation of the Cu films compared to the more conventional high temperature annealing methods without plasma, which thereby forms dense nanocrystalline phase pure $Cu_2O$ films with lower resistivity without the use of any extrinsic dopants. To the best of our knowledge this is the first report on the microwave plasma oxidation of Cu films to $Cu_2O$.

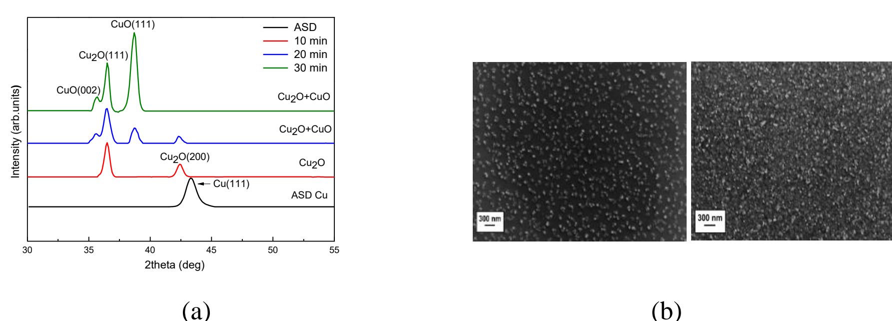
## 2. Experimental

Cu thin films of 80±5 nm thickness were deposited on glass substrates by pulsed dc magnetron sputtering of a Cu target (Kurt J Lesker; 99.99% pure). The base pressure of the sputtering chamber and the deposition pressure were $2\times10^{-6}$ mbar and $5.5\times10^{-3}$ mbar, respectively. The target was pre-sputtered for about 10 min and the distance between the target and the substrate was 6 cm. The sputtering was carried out in pure argon atmosphere. The Cu films are then transferred in to a Hitachi microwave plasma chamber for oxygen plasma exposure, in which the sample holder was kept at a temperature of 300 °C. Oxidation was performed in a 1000 sccm flow of oxygen. The chamber uses a microwave plasma with frequency and power of 2.45 GHz and 600 W

respectively. The Cu films are exposed to the oxygen plasma for different time intervals of 10, 20 and 30 minutes.

## 3. Results and discussion

Figure 1(a) shows the θ-2θ X-ray diffraction (XRD) patterns of the oxidized copper films prepared with various oxygen plasma exposure times, together with the data of the as-deposited (ASD) Cu film. The ASD sample clearly exhibits the presence of a Cu (111) peak. A complete formation of pure cubic $Cu_2O$ phase is verified from the XRD pattern of the 10 min plasma exposed film with the appearance of the $Cu_2O$ (111) and (200) peaks, with predominant orientation along the (111) direction and with no indication of other phases. These diffraction peaks are in good agreement with the standard $Cu_2O$ patterns [10]. The additional formation of the monoclinic CuO phase together with the $Cu_2O$ can be clearly seen in the XRD pattern of the films deposited at longer plasma exposures of 20 and 30 min. Efficient oxidation of the Cu films at lower temperature could be due to the supply of the portion of the oxidation activation energy from the highly energetic plasma. The increase in the intensity of the CuO (111) and (002) peaks at higher plasma exposures (30 min) can be attributed to further oxidation of $Cu_2O$ to CuO by the consumption of more oxygen from the plasma, via the possible addition of more energy to the reaction process from the longer oxygen ion bombardment sufficient for the oxidation to CuO. The oxidation of the Cu film is found to be highly controllable and the ratio of the two phases can be easily tuned by adjusting the plasma exposure time of the Cu films.




(a) (b)

**Fig.1.** (a) XRD patterns of the ASD and oxygen plasma exposed Cu films. (b) SEM micrographs of the ASD Cu film (left) and $Cu_2O$ film (right) on glass substrates.

The morphologies of the films were examined using scanning electron microscopy (SEM) analysis. Figure 1(b) shows the SEM images of the ASD film and the $Cu_2O$ film (10 min plasma exposed) with the same magnifications. The Cu film shows the presence of small grains of dimension of approx. 50 nm. Interestingly, as the Cu is exposed to the oxygen plasma for 10 min, densely packed grains of $Cu_2O$ of sizes around 20-30 nm are formed.

For short plasma treatment times the formation of the less thermodynamically stable $Cu_2O$ phase is the first stage of the oxidation. This is expected due to the relatively small amount of oxygen present for such short treatment times, and also due to the lower oxidation activation energy of the $Cu_2O$ phase [11]. While one might expect that even for short plasma treatments CuO islands would form in the Cu matrix, we believe that the greater surface energy effects at boundaries between oxidized and unoxidized Cu regions in such a case would tend to favour the formation in the first instance of larger $Cu_2O$ islands. It is also expected that the plasma could enhance both the diffusion of oxygen and the interfacial Cu oxidation rate. As plasma treatment times increase, the contribution towards the oxidation activation energy increases and the amount of oxygen present for reaction grows. The oxidized Cu can transform to the more thermodynamically stable CuO phase, with surface effects reduced as larger CuO islands are possible due to the larger amount of oxygen present. This explanation is consistent with our data shown above.

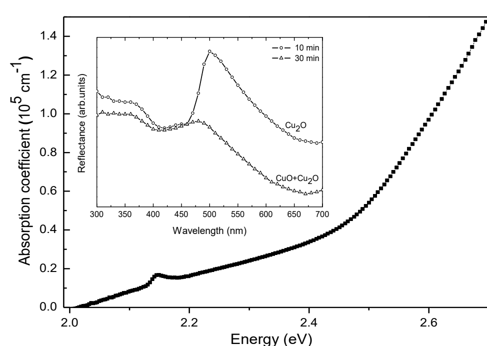



**Fig.2.** Absorption spectrum of $Cu_2O$ at 77 K and inset: Reflectance spectra of the phase pure $Cu_2O$ (10 min) and $CuO+Cu_2O$ (30 min) films.

Low temperature (77K) absorption measurement was performed on the film in order to estimate the optical band gap of the $Cu_2O$ (figure 2). The spectrum shows the band edge at 2.01 eV, with the appearance of a small peak at 2.14 eV, which corresponds to the first allowed green excitonic peak of $Cu_2O$. These values are in close agreement with the previous reports on bulk $Cu_2O$ [12]. The presence of the $Cu_2O$ phase formed during the 10 min oxygen plasma exposure can be again verified using the reflectance spectra in the inset of figure 2. The presence of the two peaks around 2.5 eV and 2.7 eV in the $Cu_2O$ sample can be observed from the reflectance spectra, which correspond to the direct allowed transitions to the n=1 exciton levels of the blue and violet series [13].

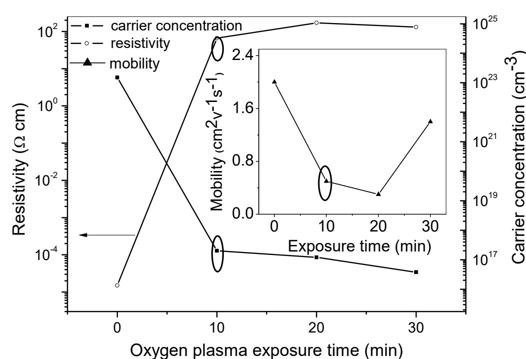



**Fig.3.** Variation of resistivity, carrier concentration and mobility (inset) plotted against the time of oxygen plasma exposure. The circled points correspond to the data of the $Cu_2O$ film.

The electrical properties of the oxidized copper films and ASD Cu were measured using Hall effect measurements and the data are plotted in figure 3. All oxidised copper films show p-type conductivity and ASD film shows n-type conductivity. The $Cu_2O$ film (10 min plasma exposed film) exhibited a resistivity and mobility of ~66 Ωcm and ~0.5 $cm^2V^{-1}s^{-1}$, respectively, with p-type carrier concentration of ~$2\times10^{17}$ $cm^{-3}$. The p-type conductivity is probably due to the presence of interstitial oxygen and negatively charged copper vacancies [14]. As the time of oxygen exposure increases to 20 min, the film comprises of both $Cu_2O$ and CuO phases, with $Cu_2O$ as the dominant phase. The resistivity increases to ~170 Ω cm, with a lower mobility and carrier concentration of ~0.3 $cm^2V^{-1}s^{-1}$ and ~$1.2\times10^{17}$ $cm^{-3}$, respectively. For the 30 min exposed sample, the dominant phase was CuO, and the resistivity decreased to ~130 Ω cm and the carrier concentration also decreased by one order of magnitude to a value of ~$3.8\times10^{16}$ $cm^{-3}$. One of the possible reasons for the relatively higher carrier

concentration (~$10^{17}$ $cm^{-3}$) and hence a lower resistivity (~66 Ωcm) for the pure $Cu_2O$ phase obtained by the present preparation method could be the increase in the presence of ionized copper vacancies as well as the densification of the film due to the bombardment by the oxygen species from the plasma. Furthermore, the lower mobility value of the pure $Cu_2O$ phase reported in the present work is attributed to the presence of increased grain boundary scattering due to the presence of nanocrystalline grains.

## 4. Conclusion

We have demonstrated a method for low temperature deposition of phase pure p-type nanocrystalline $Cu_2O$ thin films. $Cu_2O$ films with low resistivity could be a worthwhile candidate for photovoltaic applications. The present oxidation method has the additional advantage of excellent control over the rate of oxide formation of the oxides, which also could have interesting applications in heterogeneous catalysis.

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