

Dependence of solar selectivity of copper-black films on their structure, chemical composition and morphology

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The composition and morphology of anodically grown solar-selective copper-black films have been investigated using X-ray photoelectron spectroscopy with depth profiling, scanning electron microscopy and X-ray diffraction. It has been found that the films showing the best selectivity have their top layer consisting predominantly of crystalline cupric oxide (CuO). In the underlying region the dominating phase is cuprous oxide (Cu_2O) with Cu/O ratio increasing systematically towards the copper substrate. It is shown that the enhanced absorption in the solar region of the spectrum is due to the stacking of layers with graded composition and also due to the surface morphology of the film.

1. Introduction

For solar thermal collectors intended to operate at temperatures of 100°C and above, the emission losses become significant and they must, therefore, be minimized. For this purpose, good optical selectivity [1] in the absorber becomes essential. Many materials [2] have been suggested and tried for achieving this and one of them is copper oxide.

Copper oxides can be formed on a desired substrate by chemical conversion [3, 4], thermal oxidation [5], spray pyrolysis [6] and electrochemical anodic oxidation [7]. In reported work [4, 5], the optical properties have been studied extensively but characterization has not been comprehensive enough. It has been shown that the intrinsic absorption by cuprous and cupric oxide is considerably enhanced as a result of a favourable morphology developed in these films. Because the chemical composition, structure and morphology are important parameters in deciding the optical properties of the films, we have attempted, a careful characterization on these lines and the results obtained are presented in this paper.

2. Experimental procedure

The method used for the preparation of these solar selective films has been described previously [7]. The normal spectral reflectance measurements in the region 0.4 to $0.8\ \mu\text{m}$ were taken using a spectrophotometer designed and fabricated in this laboratory [8]. Total reflectance measurement in the range $[0.38$ to $0.76\ \mu\text{m}]$ was recorded with a Pye-Unicam spectrophotometer model UV/VIS SP8-100 using a reflectance attachment. Normal reflectance in the region 1 to $15\ \mu\text{m}$ was recorded using a Perkin-Elmer double beam spectrophotometer model 221 using a reflectance attachment.

Solar absorptance (α) and thermal emittance (ϵ) were recorded using the D and S (Devices and Service Co., Texas) alphanometer and emissometer, respectively.

The structure of these films was examined by electron diffraction and X-ray diffraction (Philips PW 1730 diffractometer). A Cambridge stereoscan 150 microscope was used to study the surface morphology. The analysis of the chemical composition of these films was carried out using X-ray photoelectron spectroscopy (XPS), X-ray induced auger electron spectroscopy (XAES), Auger electron spectroscopy (AES) with the help of ESCA-3, MK-II instrument using $\text{MgK}\alpha$ ($1253.6\ \text{eV}$) or $\text{AlK}\alpha$ ($1486.6\ \text{eV}$) as the radiation source. During the AES depth profile studies a multi-channel multiplex control was used for peak-to-peak height detection of Auger peaks as a function of sputtering time.

3. Results

Figs 1 and 2 show typical spectral reflectance curves obtained from passivated anodic oxide films formed

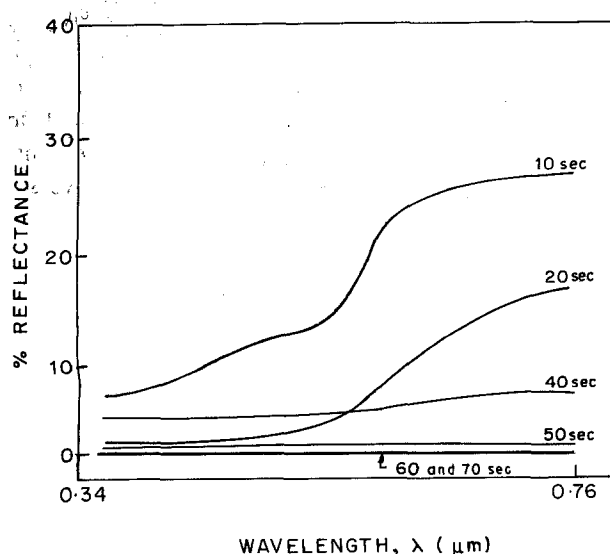


Figure 1 Effect of deposition time on the total reflectance of the copper-black film.

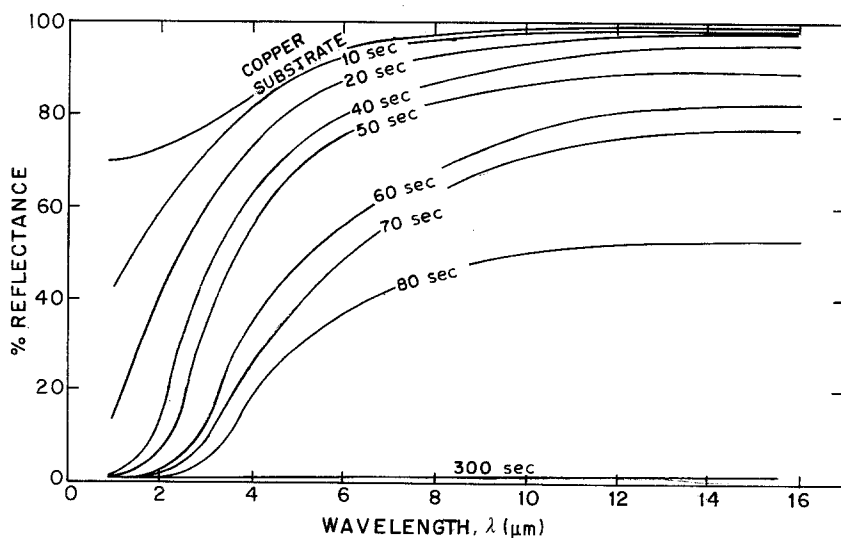


Figure 2 Effect of deposition time on the normal reflectance of copper-black film.

on copper substrate with variation in time of deposition leading to a thickness variation in the region 0.34 to 0.76 μm and 1 to 15 μm , respectively. The optimization for high solar absorptance (α) with low emittance (ϵ) is more evident from curves 1 and 2, showing that the deposition time of 60 sec is optimum. At this stage, the film thickness is between 0.15 and 0.20 μm . The normal spectral reflectance curves for an optimized time of deposition ($T_D = T_{\text{opt}}$) is shown in Fig. 3 which shows $\alpha \approx 0.96$ and $\epsilon \approx 0.2$ as reported in our earlier communication [7]. The important observations from Figs 1 to 3 are given below.

(i) The total reflectance favourably dropped with increase in the deposition time (T_D) of 40 sec, shifting the reflectance edge from 0.6 μm for $T_D = 10$ sec, 20 sec, to higher wavelengths.

(ii) The total reflectance minimization in the region 0.34 to 0.76 μm saturates after $T_D = 60$ sec.

(iii) Fig. 2 shows that the normal spectral reflectance in the region 1 to 15 μm decreases with increase in T_D or thickness. At longer deposition time ($T_D \geq 300$ sec), the film shows very small reflectance throughout the region (0.3 to 15.00 μm).

Although the films deposited for $T_D = 40$ and 50 sec (Fig. 2) show higher reflectance in the infrared region, these films have lower absorption in the wavelength region of 0.34 to 0.76 μm and hence

the calculated value of α over the entire solar region is smaller than that obtained for $T_D = 60$ sec, i.e. T_{opt} .

3.1. X-ray and electron diffraction

X-ray and electron diffraction studies on the films showed the presence of both Cu_2O and CuO as previously reported [7]. However, a detailed study showed some additional interesting observations.

(i) The X-ray diffractograms of a film with $T_D < T_{\text{opt}}$ shows CuO and Cu_2O peaks, respectively (Figs 4 and 5). As the deposition time (T_D) increases, the intensity of CuO line increases, while that of the Cu_2O line decreases.

(ii) Crystallite size for films of T_{opt} is of the order of 10 to 20 nm.

(iii) Electron diffraction studies on selective films (Table I) show lines corresponding not only to CuO and Cu_2O phases, but also to metallic copper. Because the film thickness is of the order of 0.15 to 0.2 μm , which is more than the electron penetration depth, this becomes an interesting observation.

(iv) Table I shows the d values of three strong lines observed and attributed to possible phases in the film for T_{opt} . The corresponding photographs (Figs 6, 7) show that the intensity for the line attributed to $d = 2.13$ diminishes while that of $d = 2.47$ increases (see Figs 6, 7).

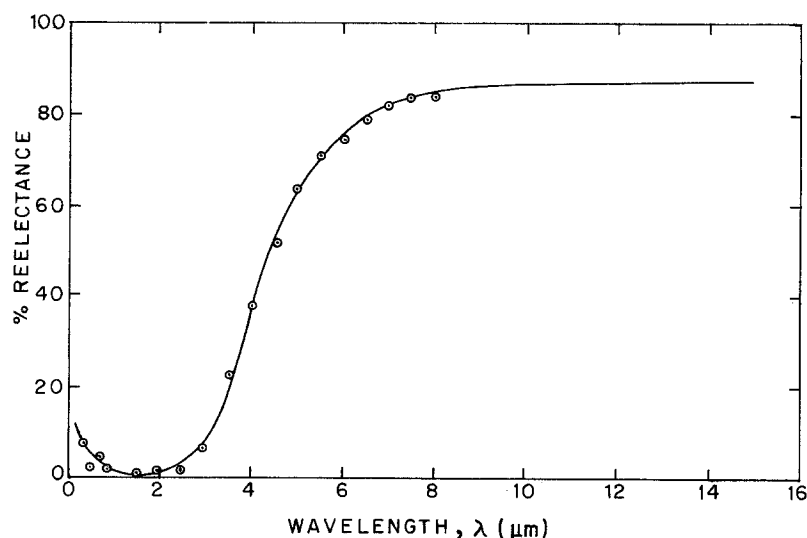


Figure 3 Reflectance of selective copper-black film (A5).

TABLE I Electron diffraction data of the selective copper-black film (A5)

| hkl | | | Intensity observed | d, observed (nm) | d, standard (nm) | | |
|-----|-------------|-------------------|--------------------|------------------|------------------|--------|-------------------|
| Cu | CuO | Cu ₂ O | | | Cu | CuO | Cu ₂ O |
| - | 002 | 111 | s | 0.247 | - | 0.253 | 0.246 |
| - | $\bar{1}11$ | - | - | - | - | 0.252 | - |
| - | 111 | - | s | 0.233 | - | 0.2323 | - |
| 111 | - | 200 | s | 0.213 | 0.208 | - | 0.2135 |
| 200 | $\bar{2}02$ | - | w | 0.183 | 0.1808 | 0.1866 | - |
| - | 202 | - | ms | 0.160 | - | 0.1581 | - |
| - | $\bar{1}13$ | - | w | 0.151 | - | 0.1505 | - |
| - | 220 | - | s | 0.137 | - | 0.1375 | - |
| - | 113 | - | - | - | - | - | - |
| 311 | - | - | w | 0.110 | 0.109 | - | - |

s, strong, ms, medium, w, weak.

3.2. XPS and XPS profiling

The XPS studies were carried out to determine the oxidation states of copper present in the film. Fig. 8 shows the copper 2P_{3/2} signal which is asymmetric and broad at 934 eV and which after deconvolution separated into two peaks, one at 932.3 eV and the other at 934.4 eV (Fig. 9). These are in agreement with the reported species [10–12], the former being attributed to Cu¹⁺ (as in Cu₂O) or Cu⁰ (as in copper metal) and the latter to Cu²⁺ as in CuO.

The XPS of the films grown with $T_D \gg T_{opt}$ is shown in Fig. 10 indicating CuO species with its characteristic intense satellite [9] at 942.2 eV. It may be noted that the peak corresponding to the Cu¹⁺ phase is not seen in thicker films.

To understand the nature of chemical species in the various regions along the thickness of the films, XPS depth profiling studies were done. The Cu2P_{3/2} peak with O_{1s} peak have been monitored.

The virgin sample shows the doublet structure corresponding to Cu²⁺ and Cu¹⁺/Cu⁰ species at their appropriate binding energies. However, as the etching

proceeds, the asymmetric peak gradually changes to a symmetrical single peak at 932.4 eV corresponding to Cu¹⁺/Cu⁰ which can be attributed to a graded composition changing from CuO to Cu₂O to metallic copper going from the outer surface towards the substrate. Thus it can be concluded that the dominant species on the surface is Cu²⁺ ion (Fig. 11a).

We have also studied the O_{1s} (Fig. 11b) peak during the profiling studies. This shows an interesting observation of continuous decrease in intensity of the oxygen peak going from the surface to the substrate, suggesting that the Cu/O ratio increases with depth.

CuL₃M₄₅M₄₅ Auger and O_{1s} XPS were also recorded. The virgin film showed the CuL₃M₄₅M₄₅ peak position (Fig. 12a) at 918.2 eV corresponding to the Cu²⁺ species [11]. It should be noted that the peak 916.2 eV corresponding to Cu¹⁺ is absent [11]. After each etching, the two peaks (Fig. 12b) corresponding to Cu²⁺/Cu⁰ and Cu¹⁺ are shown with the intensity of the latter falling going from the surface to the substrate. The peak at 918.2 eV is always broad compared to the peak at 916.2 eV, as shown for the substrate in the last

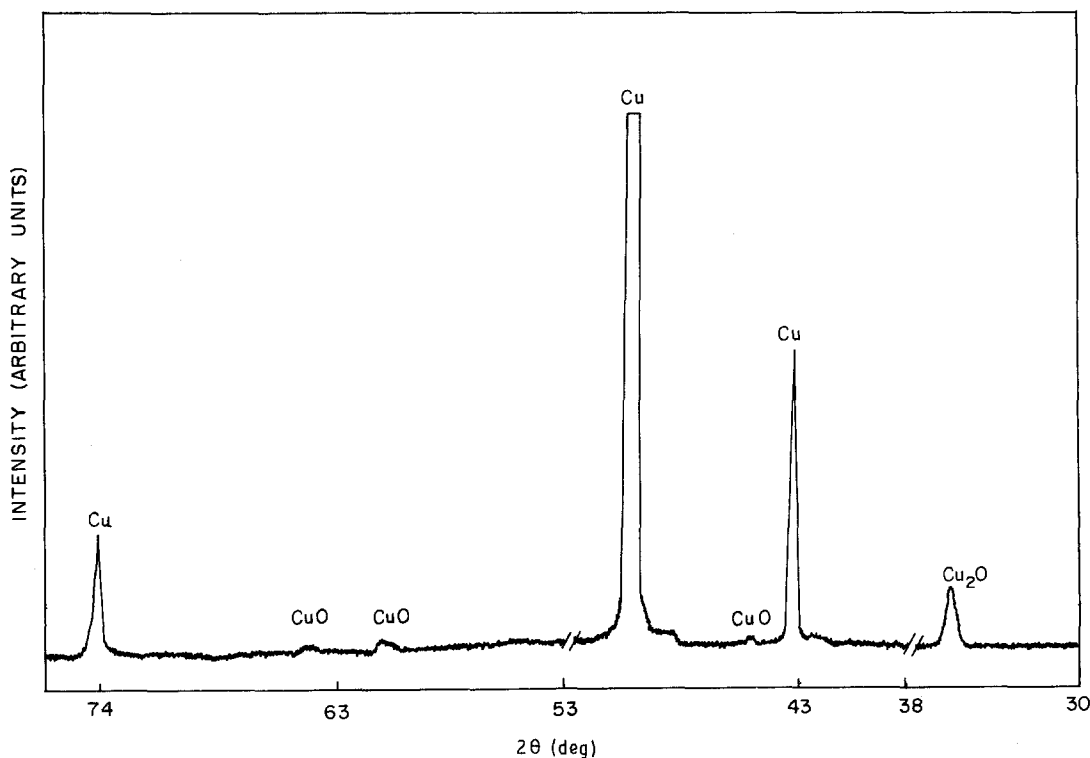


Figure 4 X-ray diffractogram for selective copper-black film (A5).

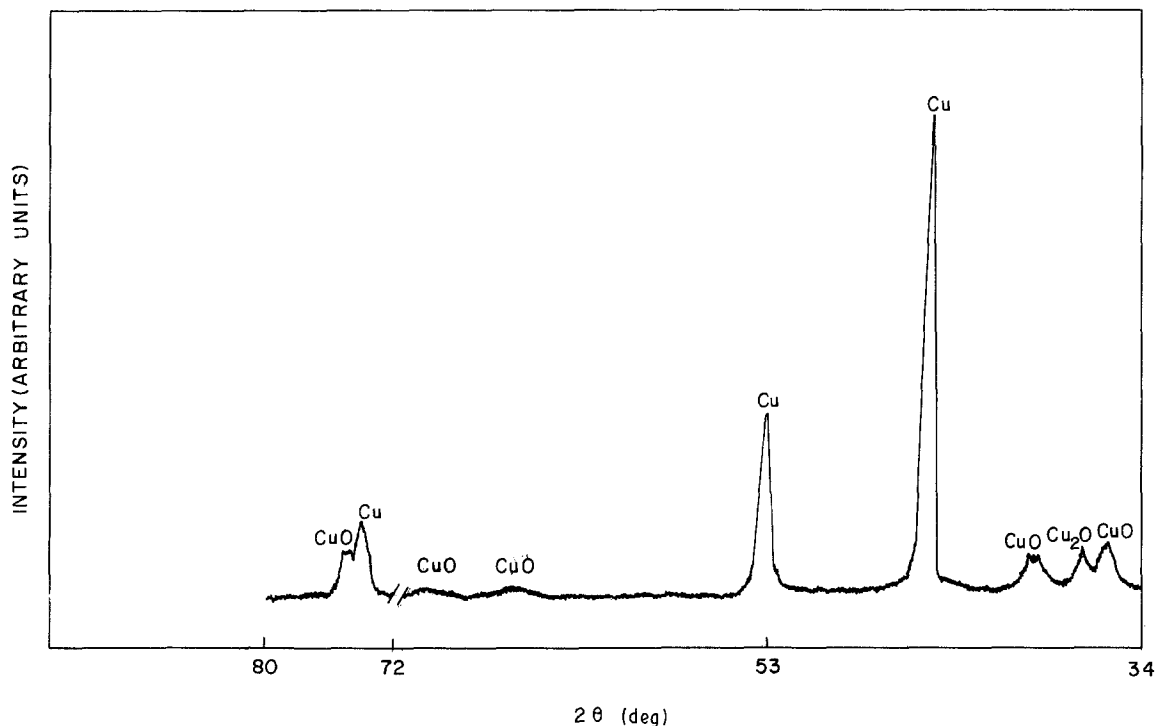


Figure 5 X-ray diffractogram of nonselective copper-black film (A6).

etching where the XPS O_{1s} signal (Fig. 11b) is totally absent. This suggests that the peak at 918.2 eV can be attributed to the presence of Cu^{2+} species along with Cu^0 which is formed due to reduction [13] of Cu_2O or CuO at the surface.

AES depth profiling study was also carried out using an electron beam as the source. The intense peak of copper $L_{3M_{45}M_{45}}$ and oxygen $OKL_{23}L_{23}$ was chosen for the depth profile study. Fig. 13 shows the peak-to-peak height as a function of etching time. The O:Cu ratio decreases continuously from 1.35 to 0.4. The higher oxygen content at the surface is attributed to adsorbed oxygen. The concentration decreases slowly, indicating the presence of an increasing amount of Cu_2O as one moves towards the substrate.

Scanning electron microscopy was used to determine the structure of the surface. Figs 14a and b show the photomicrographs for selective, i.e. T_{opt} , and non-selective, i.e. $T_D \gg T_{opt}$, films for comparison. It can be seen that the selective films have a uniform distri-

bution of particle size ranging from 0.5 to 1 μm and uniform voids of comparable size, while the nonselective films show a considerable spread in the particle size with a substantial number of particles of size greater than 3 μm and also the voids are found to be nonuniform with respect to its size and distribution.

4. Discussion

From the X-ray and electron diffraction studies, it is clear that the films consist of a mixture of crystalline CuO and Cu_2O . With increase in the thickness the rise in the intensity for the lines corresponding to CuO in both X-ray and electron diffraction points towards an increasing proportion of CuO . It should also be noted that in electron diffraction studies, known to be a surface sensitive tool, a line corresponding to metallic copper is observed suggesting the porous nature of the film. SEM studies also show a high degree of porosity in the selective films, which, of course, decreases in the thicker films.

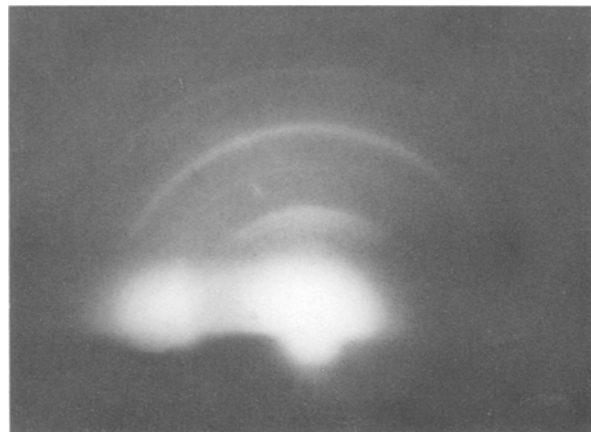


Figure 6 Electron diffraction pattern of selective copper-black film (A5).

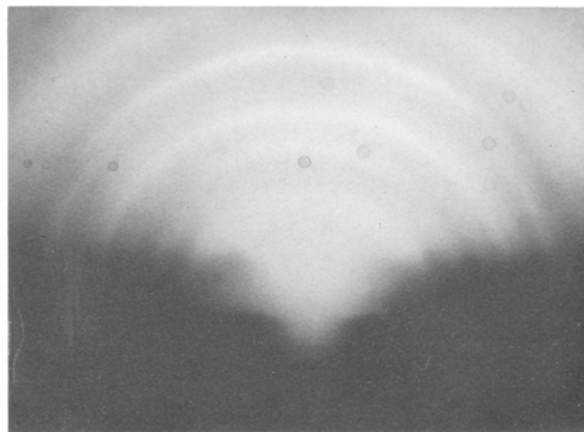


Figure 7 Electron diffraction pattern of nonselective copper-black film (A6).

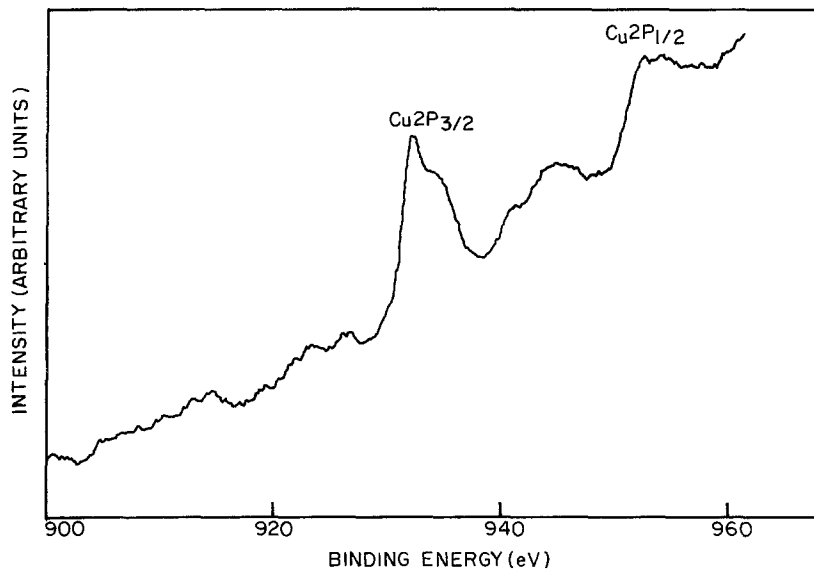


Figure 8 XPS of selective copper-black film (A5).

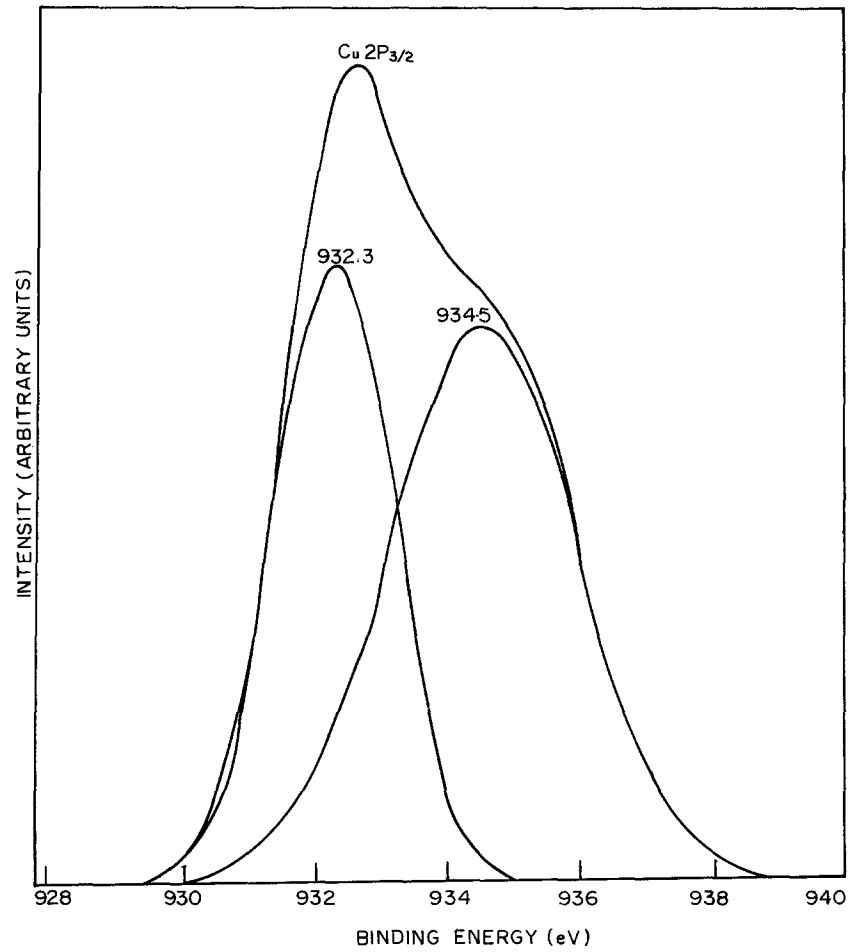


Figure 9 XPS of selective copper-black film after deconvulsion.

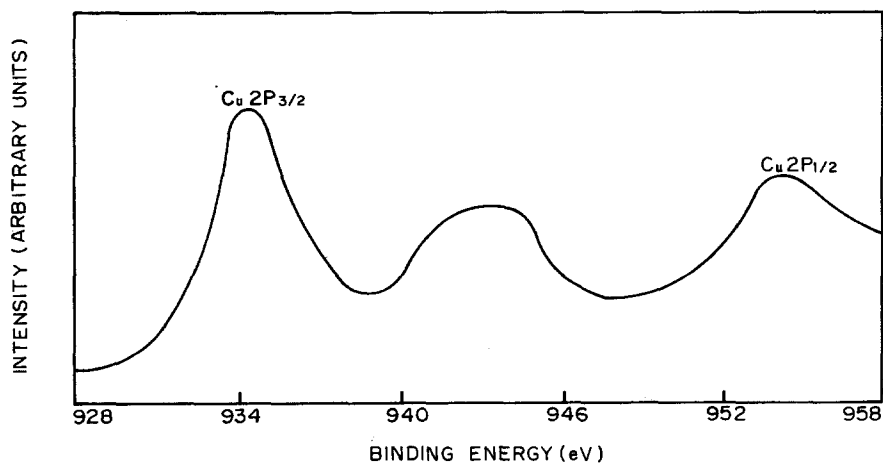
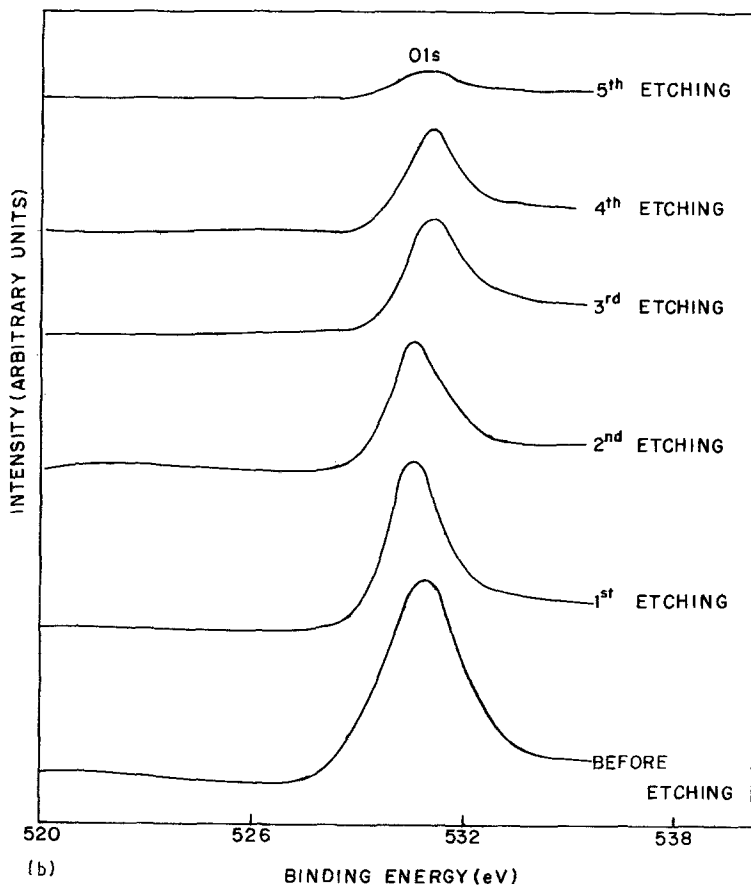
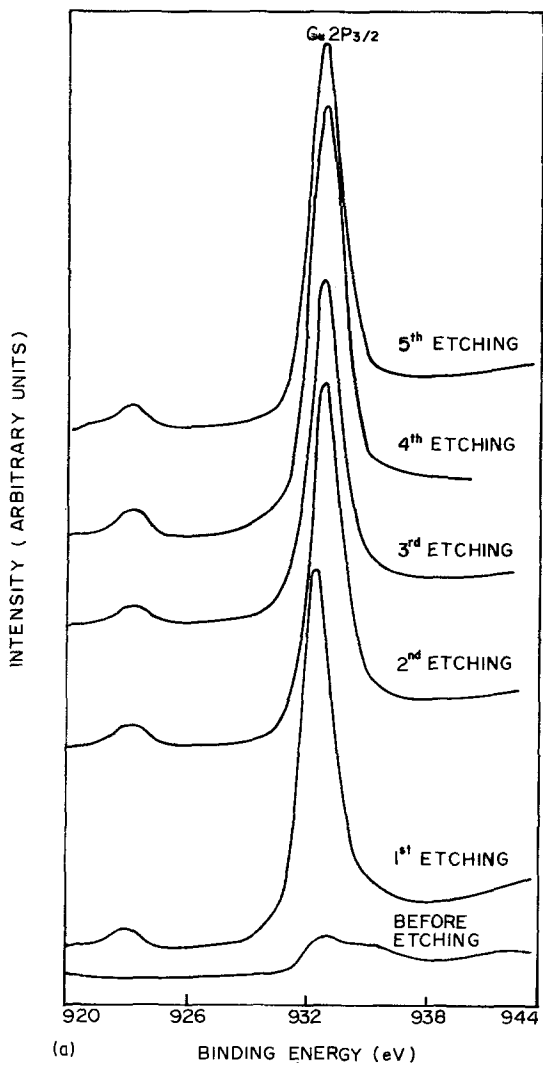


Figure 10 XPS of nonselective thicker copper-black film (A6).

Figure 11 XPS of (a) selective copper-black film (A5), and (b) XPS selective copper-black film for oxygen.



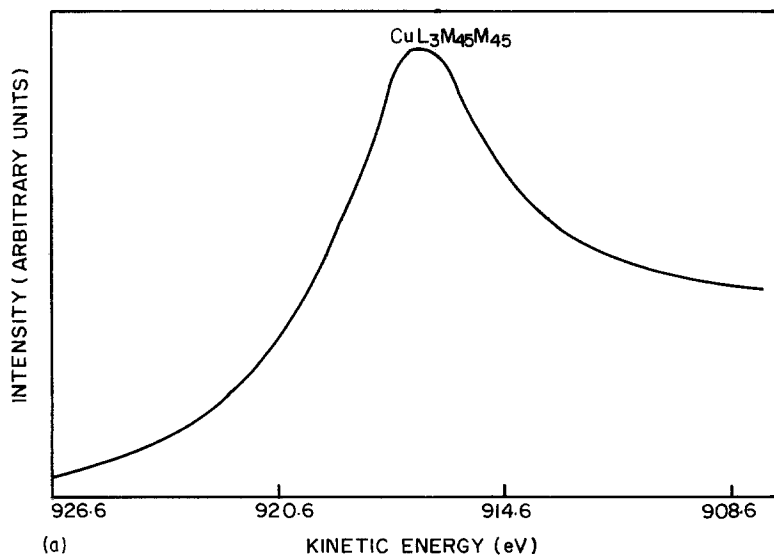
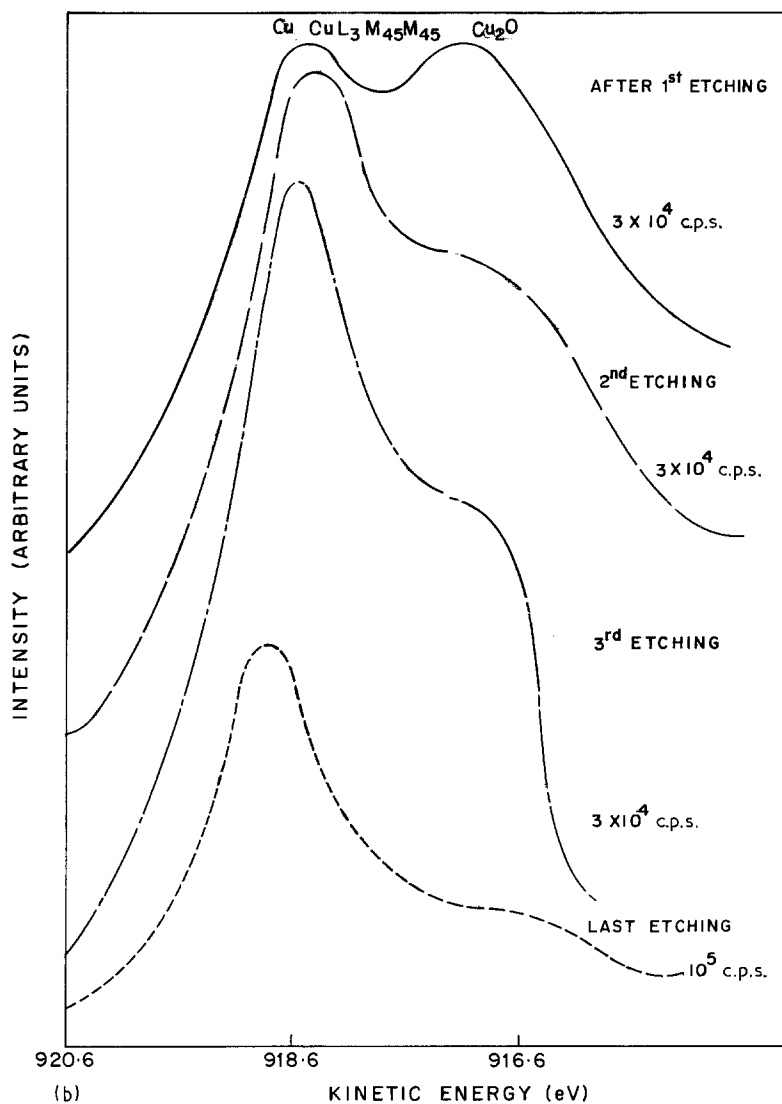


Figure 12 Auger spectra of (a) selective copper-black film (A5), and (b) copper-black film (A5).



The XPS studies on the samples with the best selectivity confirm the presence of CuO and Cu₂O/Cu species in the top layer as shown by the deconvolution of the asymmetrical peak obtained in the recorded spectrum. The XAES study also confirms this finding. In the unetched sample, the peak corresponding to Cu₂O is absent. However, in the depth profiling carried out by successive etching, curves confirm the presence of both CuO and Cu₂O phases throughout

the bulk. At the same time, the relative intensity of the Cu₂O peak compared with the CuO + Cu peak, goes down. At the same time, we know that the O/Cu ratio also decreases on going towards the substrate. This suggests the presence of more copper closer to the substrate. However, there is a possibility that this reduction could have taken place as a result of argon ion bombardment. To avoid this complication we also attempted scraping the film with a stainless steel blade

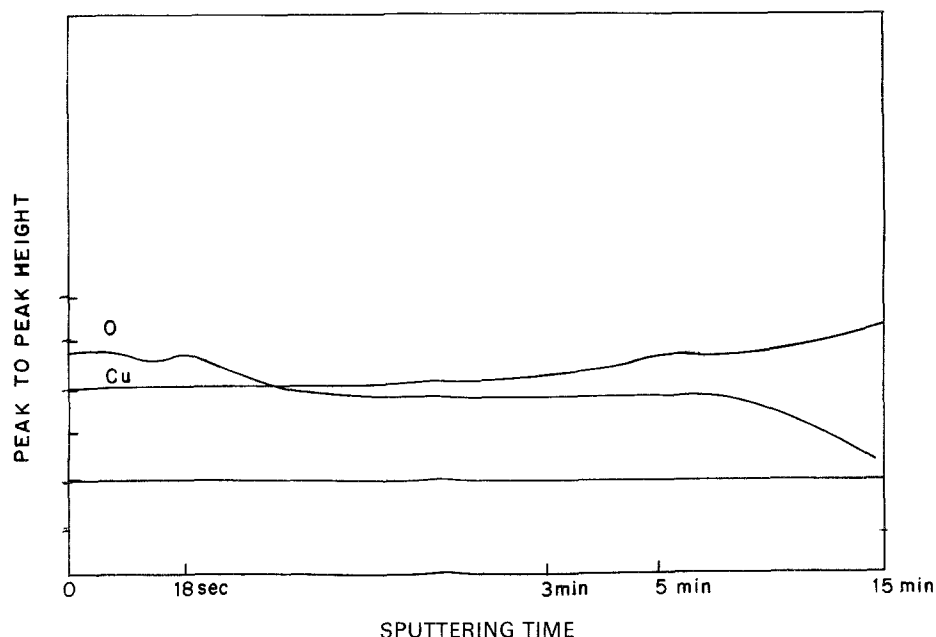


Figure 13 AES depth-profile of selective copper-black film.

inside the chamber. The results of these studies are given in Fig. 15a. The results of chemical etching of the film by very dilute hydrochloric acid and its XAES in comparison with the virgin sample are shown in Fig. 15b. We are aware that the etching rates of CuO and Cu₂O by HCl would be different. Taking this into account, the following conclusions seem reasonable.

1. The peak at 917.4 corresponding to CuO continues to exist even after etching, indicating that the CuO phase is also present in the bulk.

2. The peak at 916.8, corresponding to Cu₂O is seen in the etched sample, indicative of the presence of the Cu₂O phase in the bulk, because in such an etching process, the possibility of reduction of CuO to Cu₂O does not arise.

3. When the intensities of the CuO and Cu₂O phases in ion bombardment etching and chemical etching studies are compared, it can be easily seen that the CuO phase decreases along the bulk while the Cu₂O phase increases from top to bottom.

4. To confirm the above observations by avoiding chemical parameters we attempted mechanical etching of the virgin samples using a stainless steel blade. XAES of the etched samples showed (Fig. 15a) (i) a decrease in the intensity of the peak corresponding to CuO, (ii) indication of the peak corresponding to

Cu₂O which was absent in the virgin sample, confirmed by a broadening of the peak.

All these observations are consistent with the observations made from chemical etching studies.

Moreover, in XAES profiling, the peak corresponding to CuO is broad compared to metallic copper peak. The broadening is lowered with the number of etchings. This shows that throughout the bulk, CuO species are present with a decrease in volume fraction from top to substrate. All the above observations are reflected in AES depth profiling where the Cu/O ratio changes continuously and uniformly from top to bottom. All these observations along with the SEM studies allow us to suggest a model for the film as given in Fig. 16. Using this model we attempt to explain the reflectance-wavelength curves obtained for our films.

The intrinsic absorption by Cu₂O and CuO phases in the film plays a major part in deciding the low reflectance obtained in the range 0.3 to 0.76 μm . Cu₂O has a band gap of 2.16 eV and CuO has a band gap of 1.5 eV; it is therefore expected that radiations with wavelengths in the region of 0.3 to 0.76 μm would be absorbed by Cu₂O; and CuO would absorb at $\lambda < 0.8 \mu\text{m}$. This is shown in the curve by low reflectance in this range.

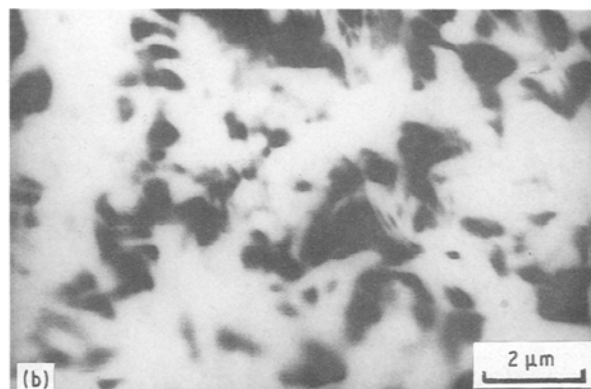


Figure 14 Scanning electron micrographs of (a) selective and (b) nonselective copper-black films (A6).

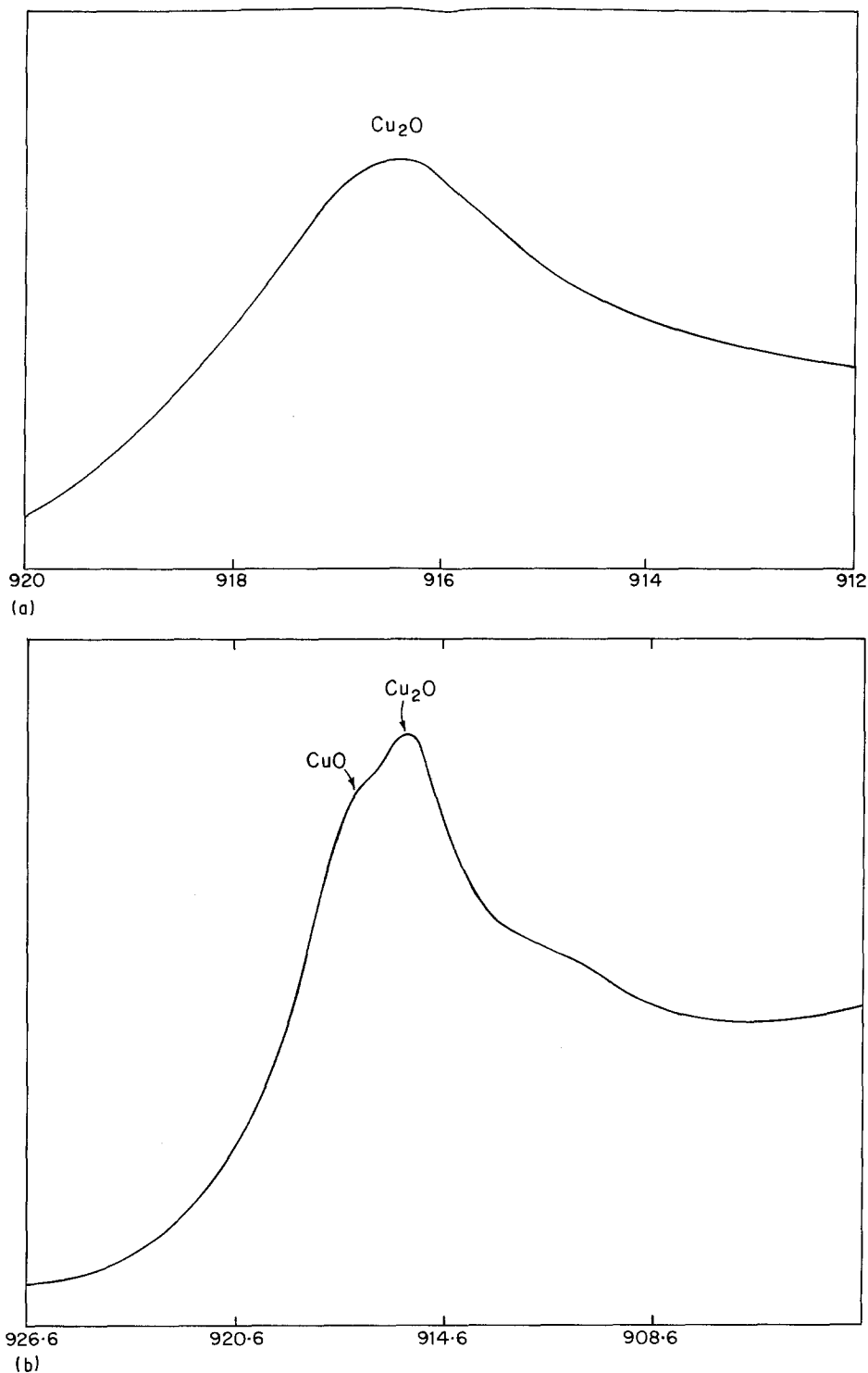


Figure 15 XAES of selective copper-black film (a) after mechanical etching; (b) after treating with dilute HCl.

From the optimization results, it is clear that when the thickness of the film is small the reflectance is lower up to $0.6 \mu\text{m}$ (curves $T_D = 10$, $T_D = 20$ sec in Fig. 1) showing the expected band edge of Cu_2O . In our model we have suggested that near the substrate, the Cu_2O phase is predominant which explains the above observation. As the thickness increases the reflectance also becomes lower beyond $0.6 \mu\text{m}$ (Fig. 1). We have shown that CuO phase increases with thickness and this causes a shift in the reflectance up to its band gap ($0.8 \mu\text{m}$) [4].

The Cu_2O and CuO will be transparent beyond their respective band gaps and therefore radiations beyond $0.8 \mu\text{m}$ would be reaching the substrate below. In other words, their reflectance would be predominantly

decided by the copper substrate used in our experiments. The polished copper substrate used gives high reflectance in the region concerned, the actual reflectance obtained is well-explained.

The absorption by CuO and Cu_2O phases based on theoretical calculations [4] cannot give α as high as that obtained in our samples. This higher absorption can be explained as due to the favourable morphology obtained for our films. The scanning electron microscope shows that a structure with uniform cavities of favourable size, causes multiple reflections to occur with increasing thickness.

The shifted reflectance cut-off shown in our optimized films is at $2.5 \mu\text{m}$. Because CuO has a λ cut-off at $0.8 \mu\text{m}$ the observed cut-off at $2.5 \mu\text{m}$ needs to be

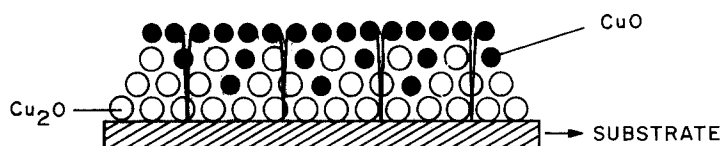


Figure 16 Proposed model for selective copper-black film.

explained. We have studied normal spectral reflectance of our films which does not include the diffused component of the radiation. Millgram [14] has given the diffused part in the region 2.5 to 10 μm . If corrections are made using this curve, the cut-off turns out to be at around 0.8 μm .

5. Conclusion

The optimized solar-selective copper-black films formed by the anodic oxidation process consist of a top layer, predominantly of crystalline cupric oxide (CuO). The underlying layer consists of crystalline cuprous oxide (Cu₂O) as the dominant phase with the Cu/O ratio increasing towards the copper substrate. The enhanced absorption in the solar region of the spectrum is due to the optimized favourable surface morphology of the films. The cupric oxide phase in the film plays an important role in increasing solar absorption.

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