JOURNAL OF MATERIALS SCIENCE 23 (1988) 3847–3853

Surface texture in electrodeposited films of cuprous oxide

A. E. RAKHSHANI, J. VARGHESE
Department of Physics, Faculty of Science, University of Kuwait, PO Box 5969, Safat 13060, Kuwait

The polycrystalline films of Cu_2O, prepared by electrodeposition, consist of grains with well-defined geometrical shapes. The size and the orientation of grains which define the surface texture can be controlled by controlling the deposition parameters. Grains with a size ranging from a few tenths of a micrometer to about 10 μm and with a preferential orientation of the (1 0 0) or (1 1 1) planes parallel to substrates can be obtained under certain deposition conditions. The effect of pH, bath temperature and the rate of deposition on the orientation and the size of grains is discussed.

1. Introduction

Electrodeposition of cuprous oxide, Cu_2O, and some prelimary results on the structure of these films have been reported [1–3]. These films were deposited potentiostatically and galvanostatically from an alkaline solution with a pH about 9. All the films deposited at this pH showed the same surface structure which consisted of four-sided pyramid-shaped grains of the order of 1 μm with a (1 0 0) preferential orientation. Further study, however, has shown that deposition of Cu_2O films with different preferential orientation and grain size is possible by controlling some of the deposition parameters such as the pH of the solution. In this paper the details of deposition of Cu_2O films having different surface structures are discussed.

2. Experimental details

Cu_2O films were cathodically electrodeposited on 0.05 mm thick stainless steel substrates at a typical temperature about 60° C. The electroplating bath consisted of a 0.1 M $CuSO_4$–Cu reference electrode (RE) and a copper counter electrode (CE). The substrates were used as working electrodes (WE). The details of deposition are discussed elsewhere [2].

The deposition solution was made up from lactic acid (3.25 M), anhydrous cupric sulphate (0.39 M) and an adequate amount of sodium hydroxide in order to adjust the pH of the solution in the approximate range of 4 to 12. The purities of chemicals were higher than 90%, 99% and 97%, respectively.

The thickness of the films was determined by a weighing method and a density of 5.9 g cm^{-3} was used for the deposits. The size of grains was measured by scanning electron microscopy (SEM). For this purpose the size of many grains observable in a scanning electron micrograph of a typical area of the film was averaged. An accuracy of 10% to 15% was estimated for the measurement of the grain size. In all SEM measurements the sample surface was normal to the electron beam.

The preferential orientation and the composition of the films were determined by using X-ray diffraction (XRD). For measuring the preferential orientation of a sample the relative intensity of the XRD peaks with respect to the Cu_2O (1 1 1) peak was calculated and the result was compared with that for a powder sample of Cu_2O. For a very weak peak which could not be detected in the XRD spectrum, its relative intensity was measured from the relative number of counts of the detector in an extended time interval.

3. Results and discussion

3.1. Structure

Films with different grain size and different preferential orientation could be deposited under different conditions. The surface texture strongly affected the film appearance. The colour of a film a few micrometres thick on stainless steel could be either light grey or dark grey. In each case the film appearance could be either matt or shiny (bright). Each of these characteristics was related to a certain structure of the film surface, as will be discussed. In all cases, films were adherent to their substrates and had a homogeneous and uniform appearance.

The films with a dark-grey colour were those which were preferentially oriented along the (1 0 0) planes parallel to substrates. These types of films had grains in the shape of four-sided pyramids having their four-fold symmetry axes perpendicular to the substrate surface. Fig. 1a shows a scanning electron micrograph and the XRD spectrum of a sample of this type. The XRD spectrum of Cu_2O powder is also shown in Fig. 1b as a standard for comparison. From a knowledge of the crystal structure of cuprous oxide, cubic with a lattice constant of 0.427 nm [4], the XRD peaks were identified and were labelled as shown. The XRD spectrum of the sample shows a strong (2 0 0) peak. The other peaks were very weak and could not be detected. By comparison with the standard spectrum of Fig. 1b, Fig. 1a reveals that the film is oriented

0022–2461/88 $03.00 + .12

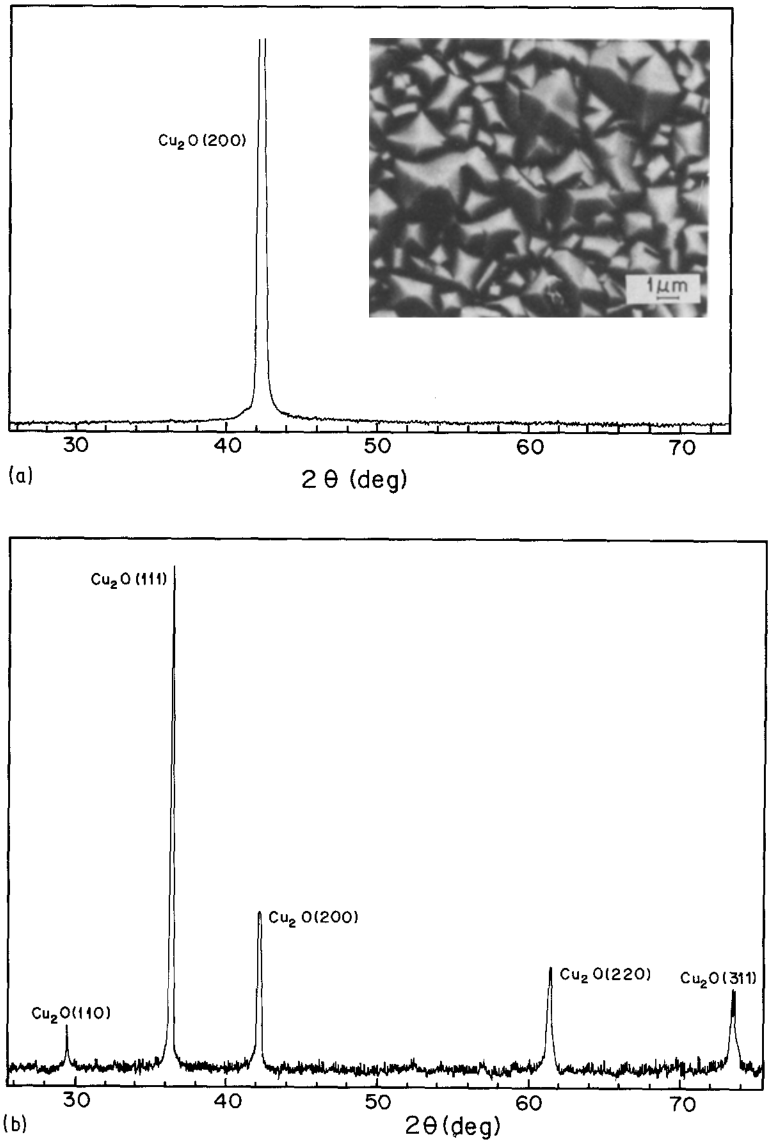

Figure 1 (a) Scanning electron micrograph and XRD spectrum of 7.7 μm Cu_2O film having a matt dark-grey appearance; (b) XRD spectrum of powder Cu_2O.

preferentially along (1 0 0) planes parallel to the substrate surface. Because the structure of Cu_2O is cubic, the four-fold symmetry axes of the grains which are perpendicular to the substrate, Fig. 1a, are expected to be the [1 0 0] directions [2], in agreement with the XRD result. The sides of the pyramids are, therefore, attributed to the (1 1 1) planes. For some unknown reasons the grains were occasionally formed in the shape of truncated pyramids. Films with large grains, a few micrometres across, had a matt appearance

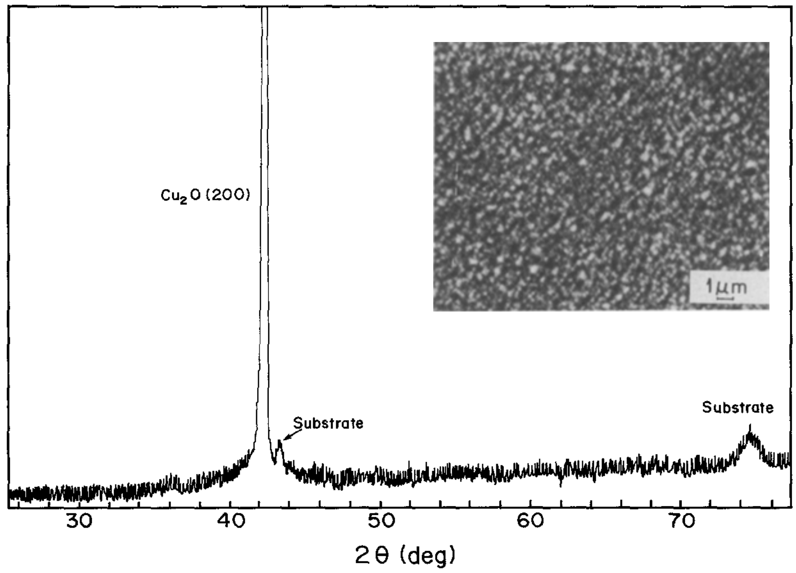

Figure 2 Scanning electron micrograph and XRD spectrum of a 3.2 μm thick, shiny dark-grey Cu_2O film.

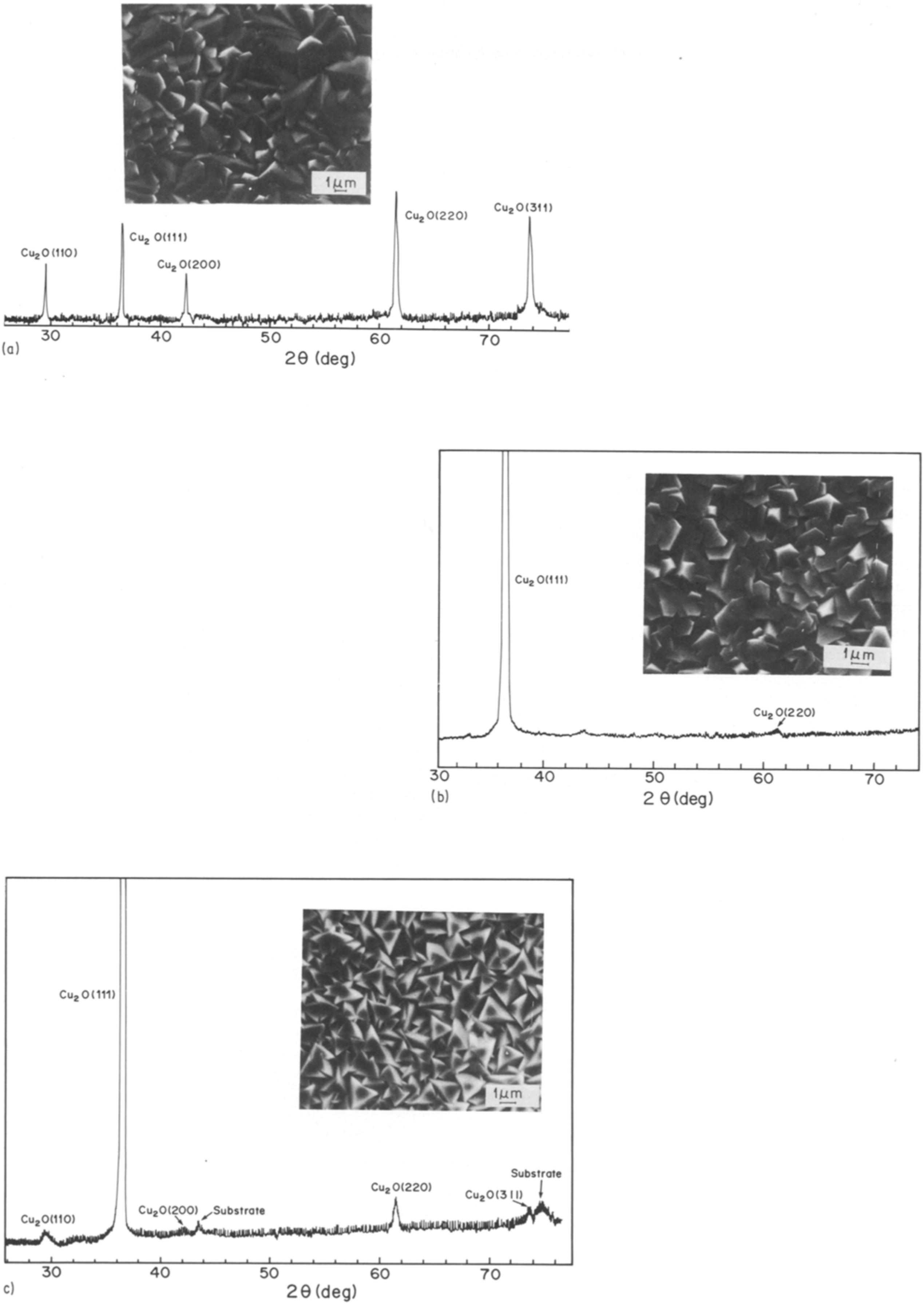

Figure 3 Scanning electron micrographs and XRD spectra of (a) 12 μm, (b) 3.3 μm, and (c) 4.5 μm Cu_2O films having a matt light-grey appearance.

while films with the same structure, but with small grains 1/10 μm, had a shiny appearance. Multiple reflection and scattering of light from the grains which are affected by the grain size determine the film brightness. The size of grains could be controlled by the rate of deposition in the galvanostatic mode of deposition as will be discussed in detail in Section 3.3. Higher rates produced smaller grains and hence

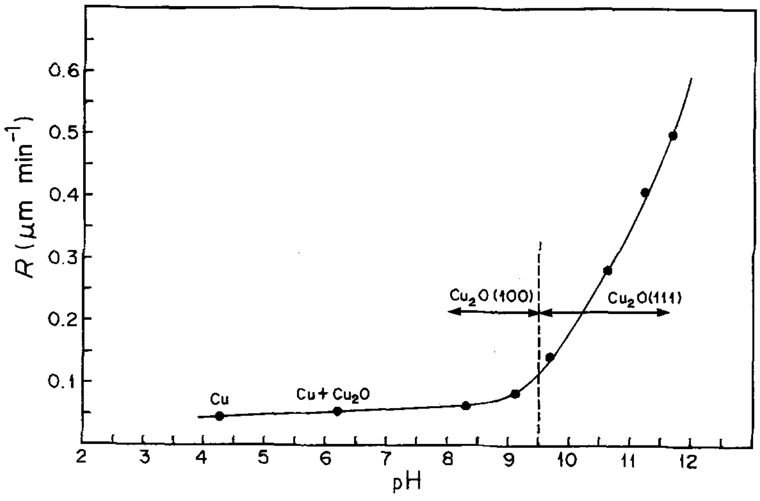

Figure 4 The overall rate of deposition, R, plotted against the pH of the solution at $T = 63°$ C; $V_{WE(CE)} = -0.470$ V.

produced films with a shiny dark-grey appearance. Fig. 2 shows the surface and the XRD spectrum of such a film prepared galvanostatically. The preferential orientation of this film is (1 0 0) which is the same as for the film in Fig. 1 though the grains are much smaller.

Films with a light-grey colour were those which did not have a (1 0 0) preferential orientation. These films consisted of grains with either a random orientation or with a preferential orientation of (1 1 1). The light-grey colour of these films had a shiny appearance if the grain size was small and had a matt appearance in the case of large grains. These films could be prepared in solutions with a pH greater than $\simeq 9.5$. Fig. 3a shows the XRD spectrum and the surface of a matt light-grey film. The XRD spectrum in comparison with that of Fig. 1b reveals that the material is Cu_2O having grains oriented in all directions but with a slight tendency towards the (1 1 0) and (3 1 1) orientations. The random orientation of grains can be seen in the scanning electron micrograph of this sample. Figs 3b and c show the XRD spectra and the surfaces of another two types of the matt light-grey films. These films, as shown by their XRD spectra, have a (1 1 1) preferential orientation. The (1 1 1) planes of the obliquely positioned pyramids are clearly observable in Fig. 3b. These planes are almost parallel to the substrate surface in agreement with the XRD result. The sample in Fig. 3c was prepared in a solution with the highest pH value (11.65) which was used. The XRD spectrum of this sample shows a preferential orientation of (1 1 1) which is in agreement with the geometrical symmetry of the grains. Grains, as can be seen, are truncated three-sided pyramids. The three-fold symmetry axes of the grains which are assigned as [1 1 1] directions are perpendicular to the substrate surface. Films of this type could be deposited potentiostatically at a very high overall rate of deposition which could be achieved using a solution with pH of 11.65. The growth of the three- and four-sided pyramids has also been observed in the electrodeposited films of metals on single-crystal substrates. For-example, deposition

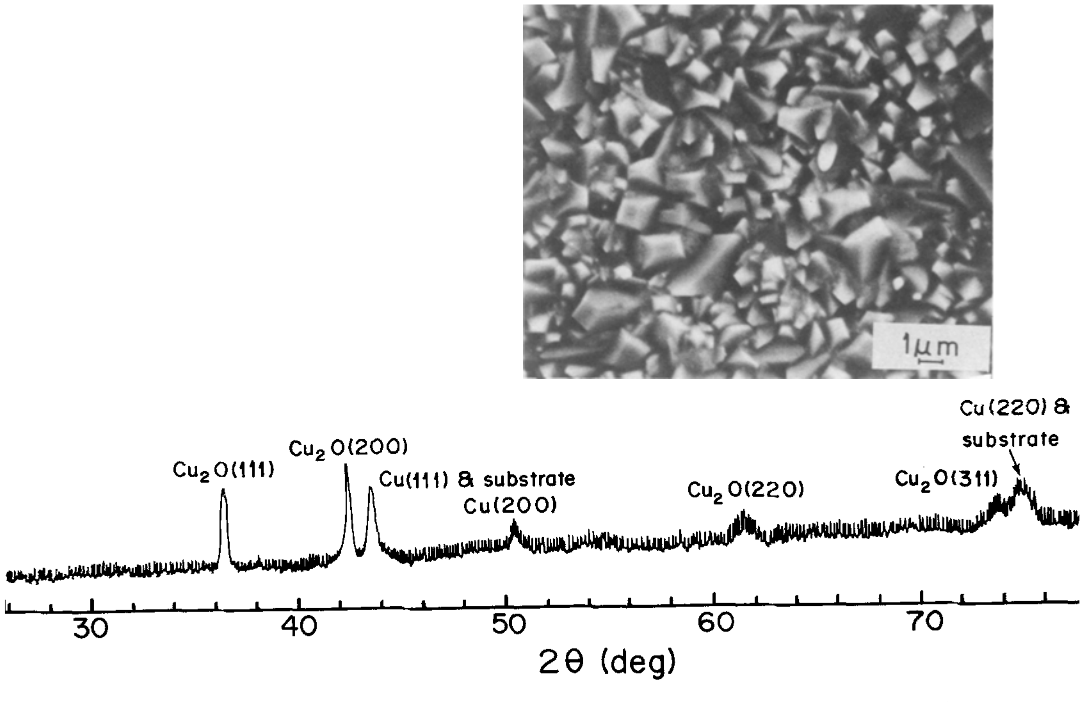

Figure 5 Scanning electron micrograph and XRD spectrum of a 2.4 μm thick film deposited at a pH of 6.2; $T = 63°$ C, $V_{WE(CE)} = -0.470$ V.

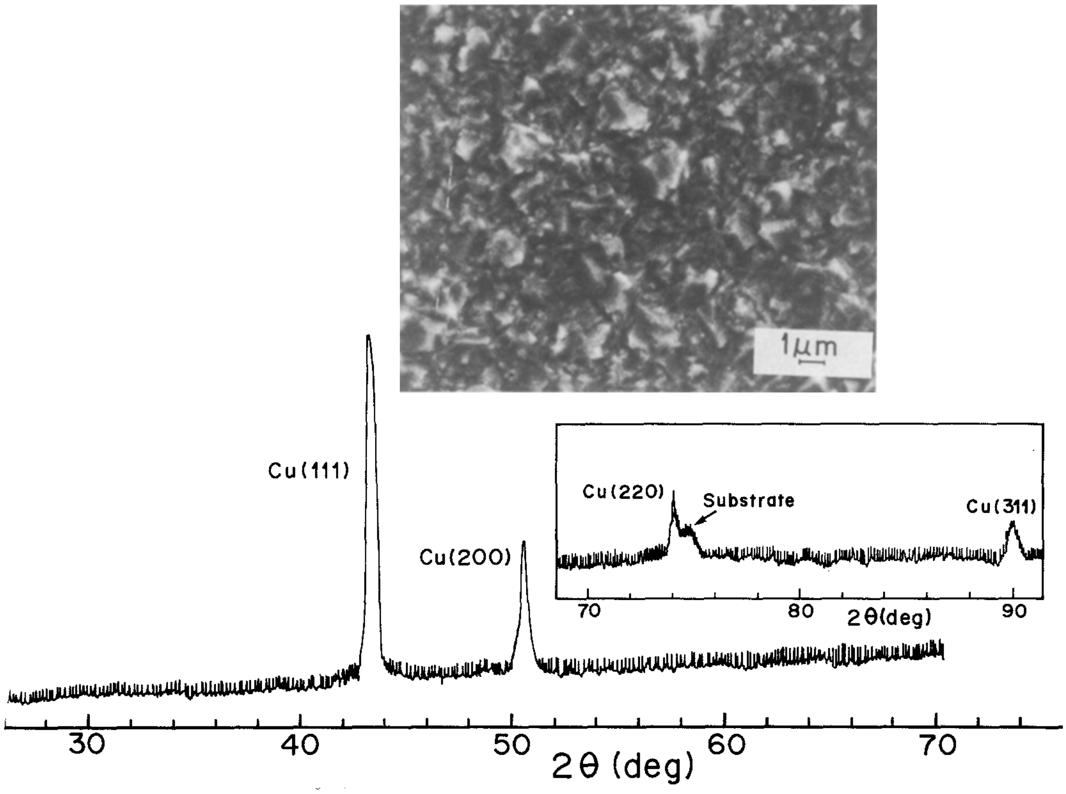

Figure 6 Scanning electron micrograph and XRD spectrum of a 2.2 μm thick film deposited at a pH of 4.25; $T = 63°\,C$, $V_{WE(CE)} = -0.470\,V$.

of copper on the (1 0 0) plane of a substrate produces four-sided pyramids, whereas deposition on the (1 1 1) plane results in three-sided pyramids [5]. This result is in support of our interpretation of the grain orientation which was discussed above.

3.2. The effect of pH

In electrodeposition of metallic films the type of surface structure depends upon the rate of deposition which, in turn, is proportional to the deposition current [5, 6]. In this study we investigated such a dependence for Cu_2O films. During deposition of Cu_2O films, at a constant WE potential, the rate of deposition does not remain constant. Initially it increases rapidly and then decays gradually as the film thickness increases. Because the instantaneous rate of deposition could not be maintained constant, the effect of the overall rate on the surface structure was studied. For this purpose films with almost the same thickness (2 to 3 μm) were deposited at different overall rates. The overall rate, R, could be changed by changing the pH of the solution, as shown in Fig. 4. In this figure all the data were obtained at a solution temperature of 63° C and at a WE potential (against CE) of $V_{WE(CE)} = -0.470\,V$. Fig 4 shows that the pH variation of R in the region of $pH < 9$, which corresponds to a low rate deposition, is negligible. In the upper part of this region ($8 < pH < 9$) the deposited films were Cu_2O with a preferential orientation of (1 0 0). As the pH was decreased further below $\simeq 8$, the film composition changed from Cu_2O to a mixture of Cu_2O and Cu at $pH \simeq 6$ and to pure copper at $pH \simeq 4$. In the latter case the film thickness and hence the overall rate of growth was calculated using the density of bulk copper, whereas for mixed films the copper content was assumed to be negligible and

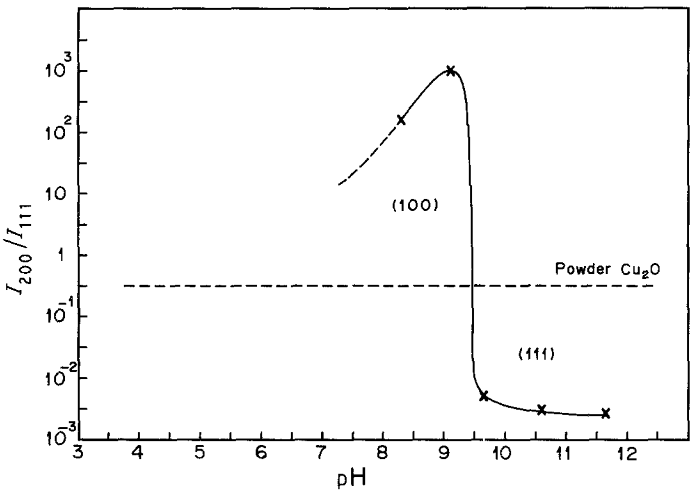

Figure 7 The pH dependence of the preferential orientation, $T = 63°\,C$; $V_{WE(CE)} = -0.470\,V$.

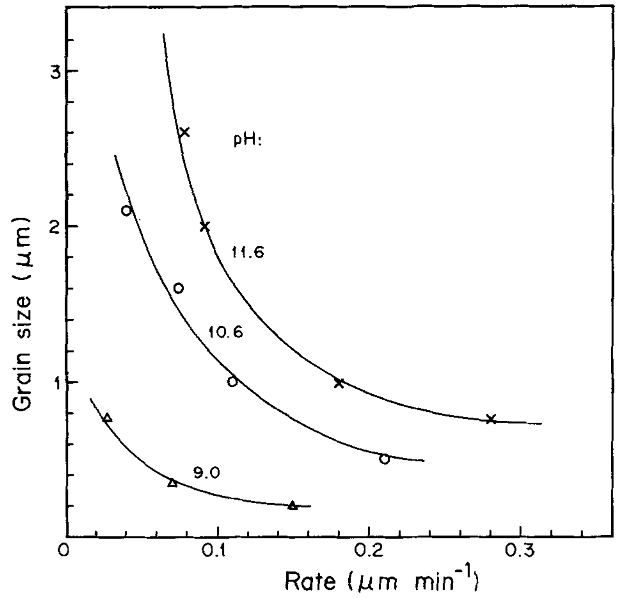

Figure 8 The effect of deposition rate on the size of grains at different values of pH; $T = 63°C$.

the density of bulk Cu_2O was used for the calculation of R.

The composition of the films prepared at pH = 6.2 was determined by the XRD method. The XRD spectrum of such a film consisted of Cu_2O and Cu peaks as is shown in Fig. 5. Two of the copper peaks, Cu(1 1 1) and Cu(2 2 0) which must appear, respectively, at 43.3° and 74.2°, overlap the two substrate peaks, though the Cu(2 0 0) at 50.5° indicates clearly the presence of copper in the film. Although the film was a mixture of copper and Cu_2O, the structure of the film was the same for the Cu_2O film with pyramid-type grains and a (1 0 0) preferential orientation. The truncated pyramids seen in Fig. 5 could also be observed occasionally in Cu_2O films with no excess copper.

The copper films with a metallic appearance which were deposited at a pH of 4.25 did not show any regular surface structure, in contrast to the Cu_2O films. Fig. 6 shows the surface and the XRD spectrum of a film of this type. This spectrum consists of only copper peaks which, in comparison with the standard XRD spectrum for copper powder, reveals that the composition of the film is pure copper without a preferential orientation. No attempt was made to determine the exact pH boundaries between the Cu, Cu + Cu_2O and Cu_2O deposition regions. However, it was determined that all the films which were deposited in solutions with pH $\gtrsim$ 8 were Cu_2O with no excess copper detectable in their XRD spectra.

The preferential orientation of the Cu_2O films in the region of pH $\gtrsim$ 8 (Fig. 4) was found to depend upon the overall rate of deposition. For pH values exceeding $\simeq 9$ the overall rate increased steeply as shown in Fig. 4. This caused the films to grow with a preferential orientation varying from (1 0 0) at pH $\lesssim$ 9 (grains as shown in Fig. 1a) to (1 1 1) at pH $\gtrsim$ 9.6 (grains as shown in Fig 3b). In an intermediate condition, polycrystalline films without a preferential orientation (grains as shown in Fig. 3a) could be deposited. As the pH was increased further beyond 9.6, the films became more oriented so that at a pH = 11.65 even the (1 1 1) symmetry could be seen in the geometry of the grains (Fig 3c). The change of the preferential orientation with pH was measured quantitatively and is shown in Fig. 7. The ratio of the intensity of the Cu_2O (2 0 0) peak to that of the Cu_2O (1 1 1) peak, I_{200}/I_{111}, was measured and plotted against the pH of the solution which was used. The value of I_{200}/I_{111} is a measure of the film preferential orientation along (1 0 0) when compared with the value for powder Cu_2O. The latter value was obtained from Fig. 1b to be 0.31. Fig. 7 shows that in a very narrow range of pH, around 9.5, films change their orientation; for example for pH < 9.1, $I_{200}/I_{111} \gg 0.31$ and for pH > 9.6, $I_{200}/I_{111} \ll 0.31$. $I_{200}/I_{111} = 0.31$ corresponds to no preferential orientation. Fig. 7 is based on the experimental results which were obtained at a typical condition, say $T = 63°C$ and $V_{WE(CE)} = -0.470$ V. However, by varying these two parameters, the overall rate and hence the value of the transitional pH is expected to change.

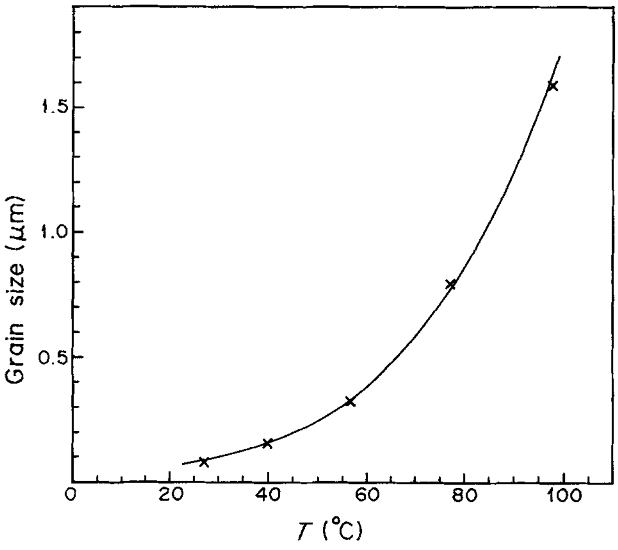

Figure 9 The effect of the solution temperature on the size of grains. Films were deposited at a constant rate of 0.030 μm min⁻¹ at pH = 8.7.

3.3. Grain size

The effect of the rate of deposition, the pH of the solution and the bath temperature on the size of grains was studied. It is known that the use of high current densities (high rates of deposition) for the deposition of materials almost invariably leads to fine-grained polycrystalline growth [5]. This was also found to be the case in deposition of Cu_2O. The galvanostatic mode of deposition [3] was used to ensure that the rate of deposition did not vary throughout an experiment. Films with different rates of growth were deposited from a number of solutions with different pH and the size of their grains was measured. The time of deposition was adjusted so that all the samples had a thickness of 2 to 3 μm. Fig. 8 shows the variation of the grain size with the rate of deposition at three pH values. As the rate increased, films with smaller grains, and hence brighter in appearance, were deposited. Fig. 2 shows the surface of such a fine-grained film which was deposited at a rate of 0.153 μm min⁻¹ from a solution of pH $\simeq$ 9. During deposition at low pH values (e.g. 9) the preferential orientation of the films remained the same, say (1 0 0), as the rate increased even beyond the limits shown in Fig. 8. For higher values of pH, however, the films showed a tendency of having a (1 1 0) preferential orientation at the rates exceeding those shown in Fig. 8. All the films which were deposited at rates exceeding those shown in Fig. 8 had surface structures which were different from the surfaces shown in Figs 1 to 3. Grains with a well-defined geometrical shape of the type shown in Figs 1 to 3 could not be detected for these films. Instead, these films showed surfaces with a spongy-looking texture. Fig. 8 shows that in addition to the rate of deposition, the pH of the solution also has an larger grains were deposited at higher pH values. At a pH of 11.65 and at a rate of $0.017\,\mu\mathrm{m\,min}^{-1}$, grains with a size of 10 to 12 μm could be deposited.

To study the effect of temperature on the size of grains, films were deposited galvanostatically at different temperatures using an electrolyte having a pH of 8.7. The galvanostatic mode was used to ensure that the change in the grain size was not partly due to the change of the rate of growth as would be the case if the films were deposited potentiostatically. All the films which were deposited in the temperature range 27 to 98° C had a preferential orientation of (1 0 0) and consisted of grains similar to those shown in Fig. 1a. The temperature dependence of grain size is shown in Fig. 9. Almost a ten-fold increase in the size of grains is measurable when temperature increases from 40 to 98° C. Films deposited at low temperatures had a shiny dark-grey colour and those deposited at high temperatures showed a matt dark-grey appearance explainable from the size of the grains.

The size of grains in the films deposited potentiostatically was found to be a function of film thickness. Thicker films showed larger grains. For such a mode of deposition this occurs because as the film thickness increases, the deposition current and therefore the rate of deposition decreases and as a result larger grains were obtained.

4. Conclusion

Electrodeposition of cuprous oxide produces polycrystalline films whose preferential orientation and grain size can be controlled through deposition parameters. The pH of the solution determines the orientation of the film and therefore the shape of the grains. The size of the grains increased with pH and temperature of the solution and decreases with increasing the rate of deposition.

Acknowledgements

The authors thank Mr A. S. Shah for XRD measurements.

References

1. A. E. RAKHSHANI, A. A. AL-JASSAR and J. VARGHESE, in Proceedings of the 2nd Arab International Solar Energy Conference, Bahrain, February 1986 (Pergamon, Oxford, 1986) p. 93.
2. *Idem, Thin Solid Films* **148** (1987) 191.
3. A. E. RAKHSHANI and J. VARGHESE, *Sol. Energy Mater.* **15** (1987) 237.
4. R. W. G. WYCHOFF, in "Crystal Structure", Vol 1 (Wiley, New York, 1965).
5. K. R. LAWLESS, in "Physics of Thin Films", Vol. 4, edited by G. Hass and R. E. Thun (Academic, New York, 1967) p. 191.
6. H. SEITER, H. FISCHER and L. ALBERT, *Electrochim. Acta* **2** (1960) 207.

Received 8 October 1987
and accepted 5 February 1988