

# The effects of surface damage and oxide films on the optical properties of cuprite

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**SUMMARY.** Spectral ellipsometry in the range 240 nm to 540 nm has been used to investigate the influence of surface damage induced by mechanical polishing and surface films of CuO on the optical properties of pure synthetic cuprite. Comparison is made between bulk CuO and thin film CuO produced by low-temperature oxidation of cuprite. The effects of strain and disorder are discussed in relation to the suppression of excitonic transitions. Recently developed techniques have been used to simplify the analysis and take full advantage of the spectral data.

It has long been known that structural defects in crystal lattices, whether point, line, or plane, have a marked effect on absorption phenomena and electronic transitions. Semi-conductors are particularly sensitive as their electrical properties are strongly affected by those defects. Cuprous oxide is a typical 'deficit' semi-conductor with a band gap of approximately 2.4 eV (Roberts and Rastall, 1978) and much investigation has been carried out into the excitonic transitions in its absorption spectrum.

Excitons are electron hole pairs in orbit produced by photon absorption in various parts of the spectrum, and their nature and properties have been discussed at length (e.g. Gross, 1962). Various workers have studied the dependence of the excitonic structure on lattice perfection. Agekyan *et al.* (1975) have shown that the method of production of Cu<sub>2</sub>O crystals strongly affects the sharpness of the exciton peaks, hydrothermally grown crystals exhibiting sharper transitions than less perfect material prepared from Cu metal by oxidation. The defect structure and stoichiometry of Cu<sub>2</sub>O is markedly affected by annealing, and Spyridales *et al.* (1977) have indicated that vacancy aggregation in bulk samples, controlled by oxygen partial pressure in the annealing process, is responsible for suppression or enhancement of the exciton peaks. Work carried out by Hayfield (1961) on thin-film Cu<sub>2</sub>O obtained by low-temperature oxidation of copper again suggests a relationship between lattice defects and optical absorption.

Experiments involving reflected light such as the ellipsometric measurements in this study are not only sensitive to bulk structural defects but are also affected by the state of the crystal surface. Surface conditions which affect the ellipsometric parameters are: (1) Surface roughness: degree of polish, presence of etch pits, grain boundaries, and scratches, etc. (2) Polish damage: disordering, increased density of the surface layers. (3) Surface film presence: incidental atmospheric contamination or controlled oxidation.

The purpose of this present study is to evaluate the effects of (2) and (3), above, on the optical properties of synthetic cuprite, and to investigate anomalously high values of the absorption index obtained in our previous study (Roberts and Rastall, 1978), which we suggested might be due to the presence of a thin absorbing surface film of CuO.

*Surface condition and etching procedure.* Specimens of pure, polycrystalline cuprite were prepared by a similar method to that described previously. After oxidation, however, the samples were not cooled slowly in a partial vacuum, but were given a separate annealing treatment of 700 °C and 10<sup>-1</sup> torr for 24 hours.

Spectral scans were carried out on an automatic following ellipsometer, the details of which are described by Roberts and Meadows (1964). The system has since been modified by the replacement of silica and glass Faraday-cell cores by water cores to reduce systematic errors and facilitate experimental procedure (Hunt, 1979).

To remove the polish-damaged layer before further measurement, samples were etched by immersing them in a mixture of concentrated nitric (20%), phosphoric (40%), and acetic (40%) acids (v/v) for 20 seconds, at room temperature. All the specimens were washed in soap solution, ultrasonically cleaned in distilled water, and dried in pure ethanol and warm air.

*Oxidation of Cu<sub>2</sub>O.* Oxidation studies, both batch and *in situ*, were carried out on polished and etched

material. Batch samples were heated in air at temperatures of 225 °C and 250 °C for various times before spectral measurements were made.

For *in situ* measurements, specimens were attached by clips to a heating element with a variable resistance control. Chromel–alumel thermocouple leads were spot-welded to the element on either side of the specimen and the apparatus was temperature-calibrated. A spectral scan was carried out before the oxidation process was started. To follow the oxidation process, the monochromator was set at 525 nm and the temperature at 250 °C. Values of the analyser and polarizer angles were recorded, ever few seconds during the initial period of rapid change and every 5 to 10 minutes thereafter, until no further changes were observed.

**Results and discussion.** Figs. 1 and 2 show the normal reflectance ( $R$ ) and  $n$ ,  $k$ , spectra for both polished and etched cuprite. The region 250 nm to 540 nm is one of high absorption with an edge at the long-wavelength end and peaks corresponding to direct allowed transitions from the  $\text{Cu}(3^d)$  levels to the conduction band (Gross, 1962). It can be seen that etching has several effects on the spectra. There is a general decrease in  $k$  except in the region of excitonic transition (445 to 520 nm) and a corresponding increase in the values of  $n$  and  $R$ . The most marked effects are the sharpening of the  $R$  peaks at 290 nm and 360 nm and a resolution of the blue and blue-green exciton series whose maxima occur at 465 nm and 480 nm respectively. There is a slight shift to shorter wavelength of the peak at 290 nm.

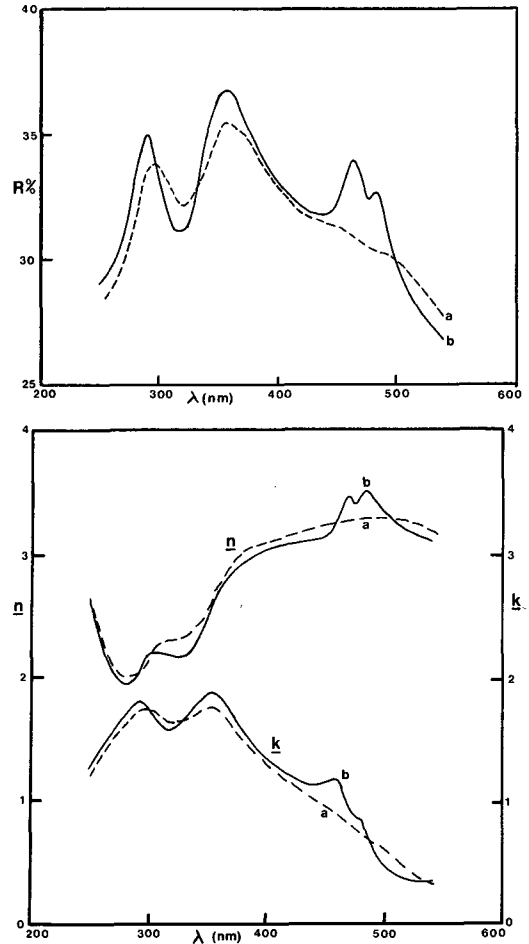
We postulate that the smearing out of the maxima is a consequence of disorder in the lattice created by abrasion of the surface layers. This is particularly apparent in the case of the exciton which can only exist in lattices displaying long-range order (some have radii of about 20 nm). At room temperature the resolution of individual members of the exciton series is not possible due to thermal broadening and the peak heights correspond to the first member of the series.

According to Gross, the radius of an exciton may be expressed as:

$$r_{\text{exc}} = \frac{\epsilon_0 h^2 n^2}{4\pi^2 \mu e^2} \times 10^{10} (\text{\AA})$$

If  $\epsilon_0$  (dielectric permittivity of  $\text{Cu}_2\text{O}$  at 465 nm) =  $11 (\times 8.8 \times 10^{-12}) \text{ Fm}^{-1}$ ,  $\mu$  (effective reduced mass of the electron) =  $0.025 m_e$  ( $m_e = 9.1 \times 10^{-31} \text{ kg}$ ),  $n$  (quantum number of the exciton) = 1,  $e$  (electron charge) =  $1.6 \times 10^{-19} \text{ C}$ ,  $h$  (Planck's constant) =  $6.63 \times 10^{-34} \text{ Js}$ , then a value of  $c. 18 \text{ \AA}$  is obtained from the first exciton member of the blue series.

Excitons are annihilated when they interact with



FIGS. 1 and 2. FIG. 1 (top). Spectral reflectance of polycrystalline cuprite. (a) Mechanically polished. (b) Mechanically polished and etched. FIG. 2 (bottom). Spectral dispersion of  $n$  and  $k$  for cuprite. (a) Mechanically polished. (b) Mechanically polished and etched.

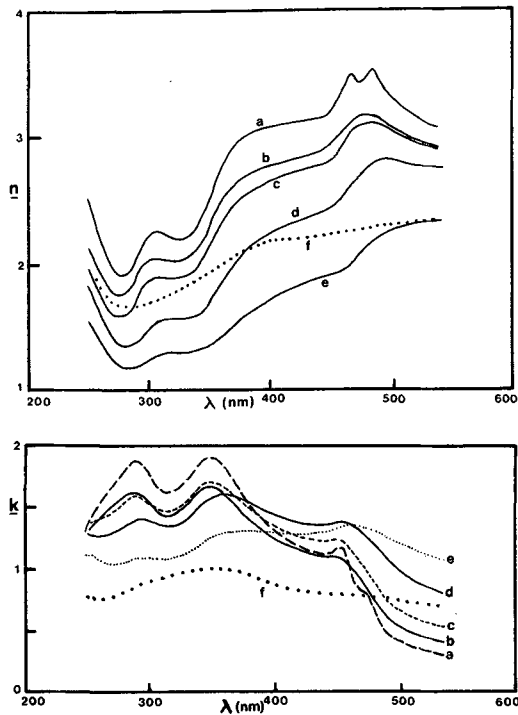
defects and the implication of these results is that the disorder induced by polishing must be extensive, the mean free path of the exciton being drastically reduced.

Other consequences of the polishing process have been investigated by several authors. Vedam and Malin (1974), who have made ellipsometric measurements on polish-damaged vitreous silica, suggest that an increased density of the surface layers occurs with a consequent increase in the value of  $n$ ; though in the case of crystalline  $\text{Cu}_2\text{O}$ , this mechanism is not possible and the change in  $n$  and  $k$  obtained here is due to disorder and an increased dislocation density in the surface which, in turn, causes a decrease in the density.

Reflectance measurements made on germanium by Donovan *et al.* (1963) suggest that apart from general disorder accompanying mechanical polishing, the surface is subjected to inelastic tensile stress which, they postulate, causes a shift to lower energies of reflectance peaks at 600 nm in this material.

The depth of the disordered layer cannot be accurately deduced from film-fitting calculations, as the optical properties of the layer appear very similar to the ordered cuprite substrate, but it is reasonable to assume that it extends to a depth corresponding to the size of the diamond particles used in the final polishing stage (250 nm). It is also likely that no sharp interface exists between the damaged layer and the rest of the crystal.

Figs. 3 and 4 show the  $n$  and  $k$  spectra for a bulk specimen of cuprite, polished and etched in the usual manner and oxidized in air at 225 °C for various times. The spectrum of CuO is shown for comparison. A gradual broadening of all the peaks is evident with each successive oxidation and the



FIGS. 3 and 4. FIG. 3 (top). Spectral dispersion of  $n$  for cuprite and CuO. (a) Mechanically polished and etched. (b) Oxidized, 225 °C, in air, 4 hours. (c) Oxidized, 225 °C, in air, 12 hours. (d) Oxidized, 225 °C, in air, 16 hours. (e) Oxidized, 225 °C, in air, 20 hours. (f) CuO. FIG. 4 (bottom). Spectral dispersion of  $k$  for cuprite and CuO under the same conditions.

value of  $k$  increases at long wavelength, with the increasing thickness of the CuO layer. As the bulk specimen of CuO was produced by a similar, though more intense oxidation process, it is expected that the continuation of the low-temperature process will produce a CuO layer thick enough completely to obscure the influence of the substrate.

Batch experiments such as the above are subject to errors in ellipsometric alignment because the films produced do not always display uniform thickness, and it is very difficult to replace the specimen in exactly the same position each time. Initial surface contamination also causes difficulty in accurate determination of the oxidation-rate law, though by repeating the first measurements at the blue end of the spectrum after completion of the scan, we have found that negligible room-temperature oxidation occurs during the experiments. Alignment errors can be eliminated by *in situ* measurements and these also facilitate monitoring of the initial stages of oxidation. The results of such an experiment at 250 °C are shown in figs. 5 and 6. Fig. 5 shows the change in the ellipsometric parameters at 525 nm as the oxidation proceeds and it is compared with the theoretical curve calculated assuming a clean substrate of cuprite ( $n'$  3.91,  $k'$  0.36) and films of CuO ( $n'$  2.35,  $k'$  0.70) of increasing thickness. The experimental curve may be divided into three parts. Part (A)

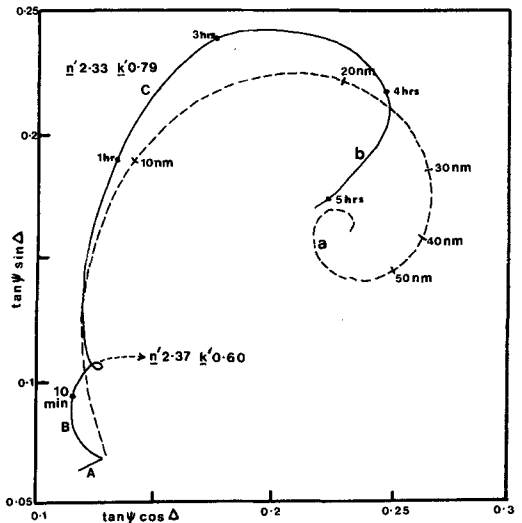


FIG. 5. Ellipsometric parameters for *in situ* oxidation of cuprite at 250 °C. Wavelength 525 nm, angle of incidence 75°. (a) Theoretical: Cu<sub>2</sub>O substrate ( $n = 3.91$ ,  $k = 0.36$ ). CuO film ( $n = 2.35$ ,  $k = 0.70$ ). (b) Experimental: (A) desorption; (B)  $n = 2.37$ ,  $k = 0.60$ ; (C)  $n = 2.33$ ,  $k = 0.79$ . [See note p. 637.]

seems to indicate an initial desorption process, or a change in the surface state of the crystal prior to any oxide growth. The rest of the experimental locus corresponds to film growth. The film appears to undergo a change when it reaches a thickness of approximately 6 nm; taking the curve as two separate loci, labelled (B) and (C), it is possible to calculate the film  $n'$  and  $k'$  for each part

$$B = n' 2.37, k' 0.60 \text{ (dashed with arrow)}$$

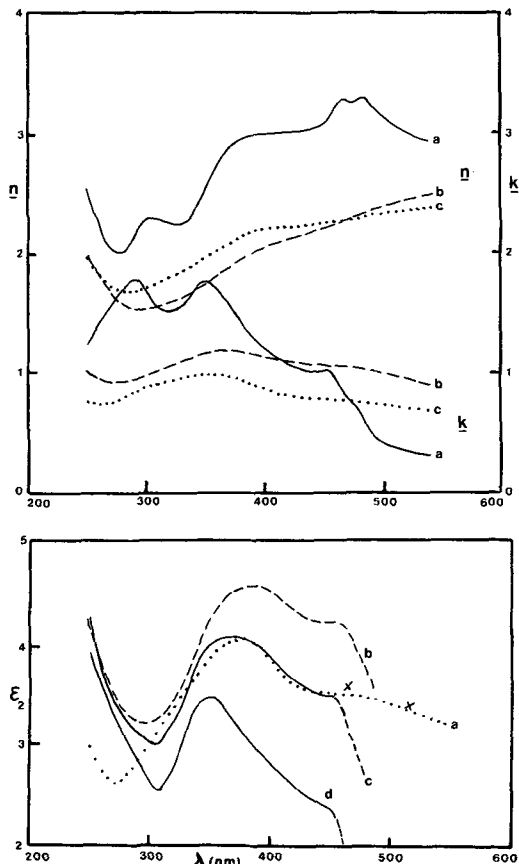
$$C = n' 2.23, k' 0.79.$$

Both these values are close to those used for the theoretical curve, though film (C) appears to be slightly more absorbing than either film (B) or the bulk CuO. Whether this change is due to re-ordering of the lattice on increasing thickness or other factors, possibly to do with surface contamination, is not known though further work in controlled atmosphere is planned.

It can be seen from fig. 6 that the spectrum of the oxidized system obtained from the *in situ* experiment at 250 °C is much closer to that of CuO than the one obtained from the batch oxidation at 225 °C but, before comparison can be made between bulk and thin film spectra, some explanation of the analytical technique is relevant.

The optical properties ( $n$ ,  $k$ ,  $\epsilon_1$ ,  $\epsilon_2$ ) of bulk specimens were derived assuming these were isotropic, homogeneous, plane, and free from surface contamination. These assumptions enable film-fitting computations to be used without serious error. The calculation of the complex refractive index ( $n-ik$ ) of a surface film from ellipsometric data must be done by iteration, as analytical methods cannot be used. If an independent measure of thickness is available,  $n-ik$  may be obtained directly from a knowledge of  $\Psi$  and  $\Delta$ . Conversely, if  $n-ik$  is known for the film, a unique value of its thickness may be determined. Without an independent thickness measurement additional ellipsometric data are necessary. One approach is to make spectral measurements and choose the refractive index, absorption coefficient, and thickness which give calculated values of  $\Psi$  and  $\Delta$  which most closely match the experimental data. Least-squares analysis is then used to perform the matching automatically, fitting the film  $n$  and  $k$  for various trial thicknesses. This is done by minimizing a function of the difference between calculated and experimental parameters (Clarke, 1979). The shape of the spectra and the magnitude of the absorption vary with the assumed thickness. The results of this operation are shown in fig. 7, the computed film spectra giving a probable value of 27 nm for the CuO film, grown *in situ* at low temperature.

It is clear that a good match between the spectra is possible only over a limited region (300 to



FIGS. 6 and 7. FIG. 6 (top). Spectral dispersion of  $n$  and  $k$  for *in situ* oxidation of cuprite. (a) Polished and etched. (b) Oxidized *in situ* at 250 °C. (c) CuO. FIG. 7 (below). Spectral dispersion of  $\epsilon_2$ . (a) Experimental CuO. (b) Least squares analysis thin film of CuO assumed thickness 35 nm. (c) Assumed thickness 27 nm. (d) Assumed thickness 20 nm. Crosses are for thick-film CuO (Ladelfe, *et al.*, 1972).

450 nm); this region in fact being dominated by just one Cu<sub>2</sub>O absorption peak. The ellipsometric results for CuO films, however, depend not only on the assumed thickness but also on the assumed substrate (Cu<sub>2</sub>O) spectrum which indicates caution when interpreting these results. In performing the film-fitting operation we have also assumed the film properties to be identical to those of the bulk material; no account has been taken of possible differences of structure between them. Structural analysis of CuO films by other methods would be of use, but apart from measurements made by Ladelfe *et al.* (1972) at 450 nm and 500 nm (fig. 7), we have been unable to find any previous work on the optical properties of CuO in this wavelength region (fig. 7).

In the light of these results it is possible to offer an explanation for the anomalously high absorption index ( $k$ ) obtained in previous work. Air-formed films of CuO on Cu<sub>2</sub>O require temperatures somewhat above ambient to reach a thickness accurately determinable by the methods employed here; however, when experiments are carried out at atmospheric pressure, some adsorption of oxygen into the surface layers is inevitable. Fig. 5 demonstrates the complex nature of the initial stages of the oxidation process.

We have also demonstrated that the surface is easily disordered and strained by preparative treatments and that this disordered layer displays abnormally high absorption at long wavelengths.

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[Note added in proof. FIG. 5. The film thickness values on the experimental curve should be doubled. i.e. for 10 nm read 20 nm, etc.]

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