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DEFECTS IN CUPROUS OXIDE SINGLE CRYSTALS

By

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Abstract. *Cuprous oxide single crystals were prepared by the grain growth method. The crystals showed a low density of normal dislocations with Burgers vector a < 110 > and a < 100 >. Dislocation loops, produced by the prismatic punching mechanism, were observed as a result of the crystal quenching. Rectangular misoriented areas producing rotation Moirè fringes were also evidence. Therefore, large areas of the crystals should be considered as having a mosaic structure.*

1. INTRODUCTION

Cuprous oxide is one of the first semiconductors which have been used for photovoltaic cells. The theoretical efficiency is about 20% but the actual one has never exceeded 1%. One reason for the poor efficiency is that the electrical properties of Cu_2O are greatly influenced by the degree of perfection of the crystalline structure. Most of the early investigations on Cu_2O were conducted on single crystals grown by the grain-growth method of polycrystalline sheets [1]. This method has the advantage to produce, in a simple and economical way, large single crystal sheets suitable for photovoltaic cells. From this point of view it would be useful to study the microstructural defects of Cu_2O single crystals prepared by this method.

Cuprous oxide has an unusual crystal structure (Fig. 1). The oxygen ions are ordered on a body-centered cubic lattice, while the copper ions occupy the sites of a face-centered cubic one. The structure consists of two completely interpenetrating frameworks, displaced by 1/4, 1/4, 1/4 of the unit cell.

2. EXPERIMENTAL PROCEDURE

Single crystals (5cm × 1cm × 0,8cm) were produced after oxidation of Cu 5N by the grain growth method. The quenching of these

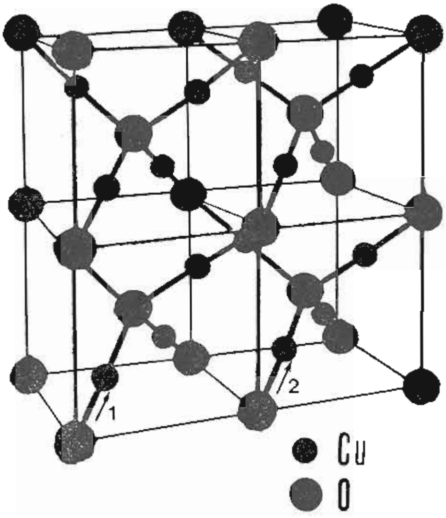

Fig. 1. Structure of Cu_2O.

crystals from 1020°C to room temperature results in the formation of a surface film of CuO. Another disadvantage is that the crystals contain an inhomogeneous region lying in a plane through the center of the plate parallel to the surface. This region can be explained by the oxidation mechanism. In fact it has been shown that copper oxidizes by the diffusion of copper to the surface where it combines with oxygen, so that a large number of very small spherical voids appear in a narrow region, at the center of the plate parallel to the surface. Toth et al. [1] have shown that this region must be removed if a reasonably uniform specimen is desired. Single crystal specimens, suitable for the electron microscope were prepared after the removal of the inhomogeneous center region and the CuO film at the surface. For this reason, the crystals were first polished using abrasive paper, until half the thickness was removed. Then the specimens were chemically polished up to 0.3mm by a solution of 1% KCN in water. After that discs 3mm in diameter were cut with a drill. These discs were further polished by a 0.5% KCN solution in an apparatus by convection jet [2]. The progress of the thinning was followed by observing the colour of the specimen. When the thinned area became pale yellow, indicating a thickness of about 0.3μm, thinning was continued by ion bombardment (5keV Ar ions) until a hole was perforated. Observations were made using a JEOL 120CX electron microscope.

3. RESULTS AND DISCUSSION

Electron microscope observation showed a low density of dislocations. From contrast experiments dislocations with Burgers vector either $\alpha < 110 >$ or $\alpha < 100 >$ were identified. The density of isolated dislocations was astimated as below $10^6 cm^{-2}$.

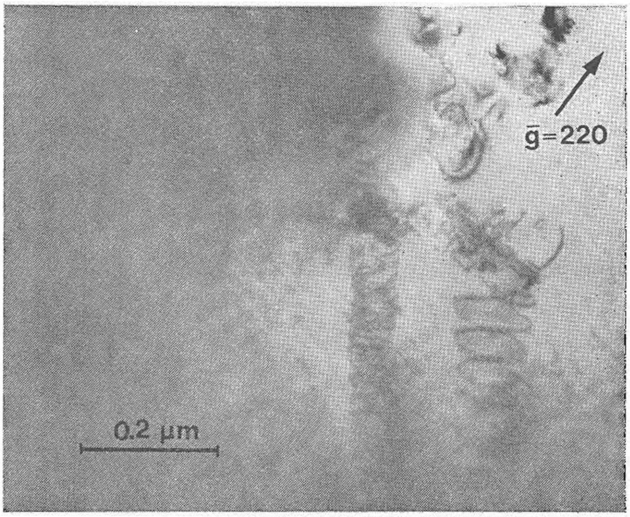

Fig. 2a.

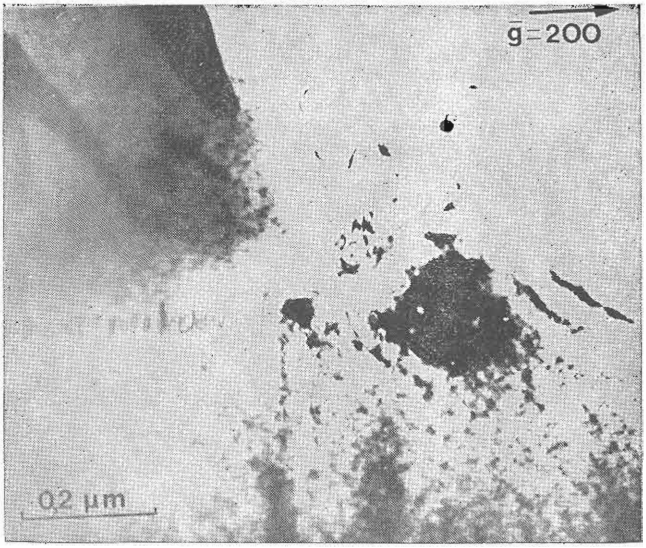

Fig. 2. Prismatic punching in a specimen with (001) orientation. Spiral and loop rows have propagated in the two <100> directions in the plane of the foil.

Although cuprous oxide specimens were produced after oxidation of 5N copper, a large number of inclusions was evident. These inclnsions were followed by a procession of loops (Fig. 2, 3). These loops have been produced as a result of the prismatic punching mechanism during the quenching of the Cu_2O crystals where the precipitates have

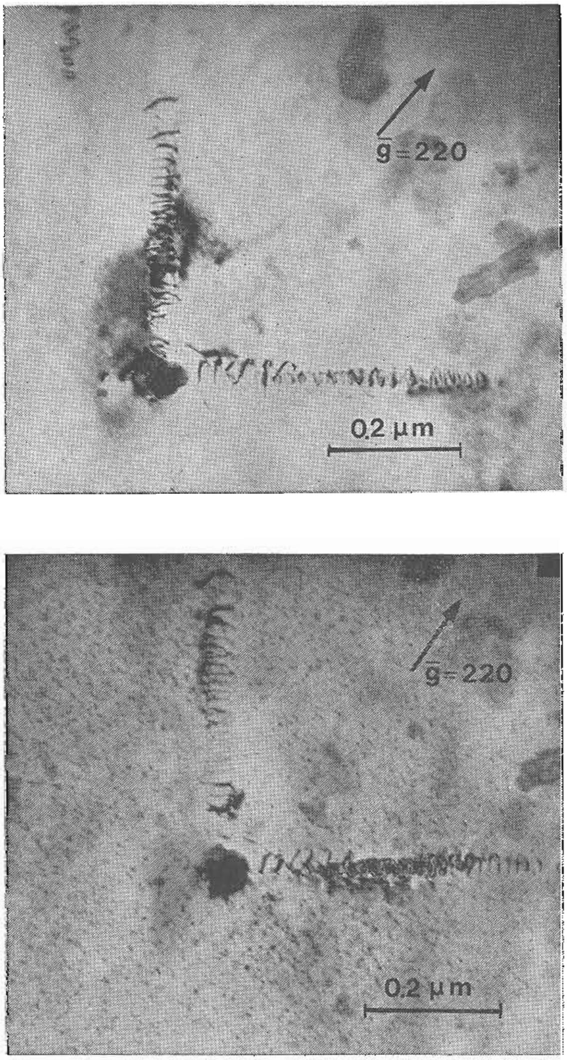

Fig. 3. a) Rows of loops propagated along [100] and [010]. b) The same photograph under the same diffraction conditions 20 min later, after a sequence of tilting experiments. Point defects due to the electron beam irradiation are evident.

been grown [3, 4]. Stresses produced by differential expansion or volume change of precipitates during cooling can be relieved by the generation of prismatic dislocation loops at the glide cylinder surface. The axis of the loops is parallel to the $<100>$ directions which is the principal slip direction in cuprous oxide [5] while the Burgers vector of the loops was $\alpha < 100 >$ (Fig. 2(a, b)), since this is the shortest distance for structural identity.

Two kinds of inclusions can be produced during the quenching of the Cu_2O single crystals precipitates of cupric oxide or precipitates of copper. Unfortunately it was impossible to identify the nature of the inclusions from selected area diffraction patterns because the intensity contribution from the precipitates was too low. Moreover, previous TEM and SEM observations on cuprous oxide revealed the presence of both CuO and copper as well [6-8]. Also, Goulden [9] has observed a similar prismatic punching during in situ observations of the growth of cuprous oxide islands on copper as a mechanism relieving part of the strain of the islands.

The outer loops are smaller than the inner ones (Fig. 2). This can be explained if we think of interstitial loops, to which vacancies are diffused during the quenching, decreasing their diameter. Sometimes a continuous helix of the same overall dimensions as the loop row was observed, its envelope tapering away from the precipitate. To estimate the differential radial expansion coefficient $\Delta a = (\alpha_2 - \alpha_1)$, it is supposed that the misfit due to the differential contraction during quenching is relieved by the generation of n loops from a precipite of radius r, where the row of loops is parallel to the surface; then

$$\Delta a \,.\, r \,.\, \theta = n \,.\, b \qquad (1)$$

where θ is the temperature difference and b the Burgers vector. Our precipitates have a value of $r = 500$Å, which have a number of $n = 15$, with $\theta = 1000^\circ C$ and $b_{100} = 4.3$Å equation (1) gives $\Delta a = 2.3 \times 10^{-4} K^{-1}$ This number is high compared with the linear expansion coefficient of Cu_2O, $a_2 = 0.93 \times 10^{-6} K^{-1}$. Since we prepared our Cu_2O by oxidation of 99.999% copper the precipitates should be cupric oxide or copper. Probably the presipitates grow during quenching, due to an eutectic decomposition of the form $Cu_2O \rightarrow CuO + Cu$ [8].

Another «defect» was the small rectangular areas bounded by well defined edges along the [100] and [010] crystallographic directions

(Fig. 4(a)). The length of the edges was between 250Å and 700Å. Parallel fringe patterns were observed frequently on these regions. Specimen tilting experiments revealed that these fringes not only changed their directions with the variation of the diffraction condition but sometimes disappeared completely.

In Fig. 4(a) the operating reflection was the 220 (Fig. 4(b)). The direction of these fringes is almost parallel to the strongly excited diffraction vector. From the above mentioned facts it is clear that these fringes are pure rotation Moirè patterns.

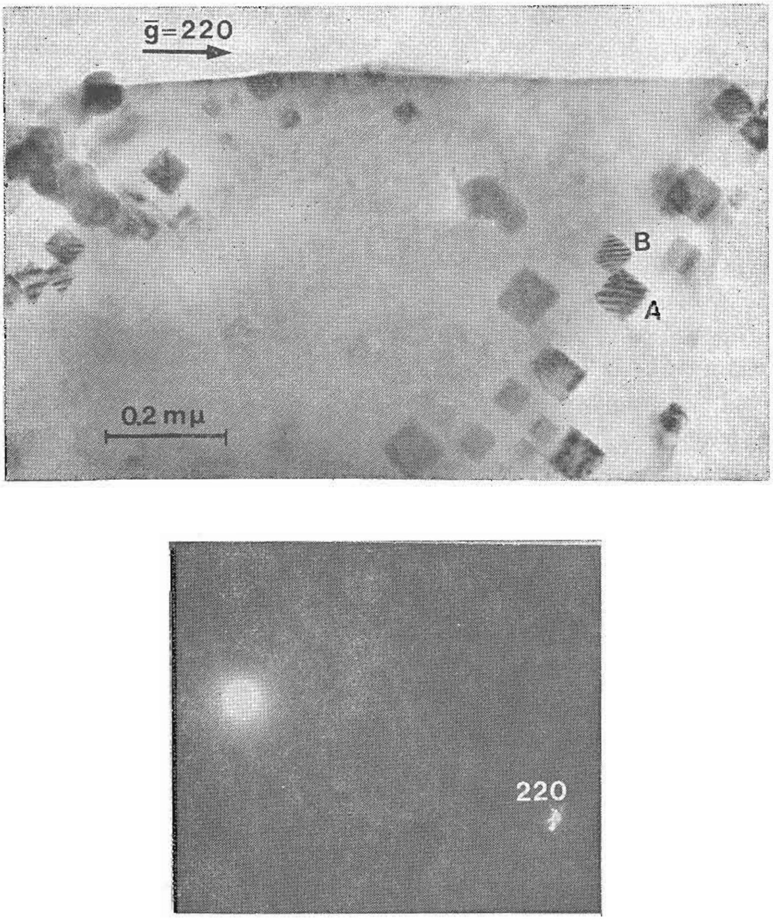

Fig. 4. Specimen close to (001) orientation. a) Rotation Moirè fringes are evident. b) Selected area 220 diffraction pattern from rectangles A and B. A tangential splitting of the diffracted intensity is evident.

By measuring the Moirè spacing D it is easy to calculate the angle of rotation according to the formula $D = \frac{d}{\varphi}$, where d is the spacing of the lattice plane. This result is in agreement with the tangential splitting of the diffracted spots 220 of Fig. 4(b).

The rectangles had different angles of rotation compared to the matrix which were easy to be calculated by measuring the Moirè spacing D. Thus in Fig. 4(a), if we consider the lattice space d = 1.51Å for the operating reflection 220, we will find a rotation of 0.25° for the rectangle A, while for the rectangle B the rotation is 0.3°.

Regions with high density of rectangular defects (Fig. 5) show irregular Moirè fringes that reveal not only a rotation but also a difference in the lattice parameters between the defect regions and the matrix.

Stereo photographs (Fig. 6) show that most of the square defects are on the surfaces of the specimen although in areas A, B and C of the photographs, a depth distribution of the defects is evident. This is because the rectangular defects are not so sensitive to chemical polishing. Points C and D in Fig. 7 are partly out of the edges of the specimen while Moirè patterns appear only in the overalapping part of the rectangles with the matrix. This fact excludes the possibility these areas to be produced by accumulation of high concentration vacancies due to the diffusion of copper to the surface during oxidation. If it was due to the vacancies concentration, a negative strain field should arise

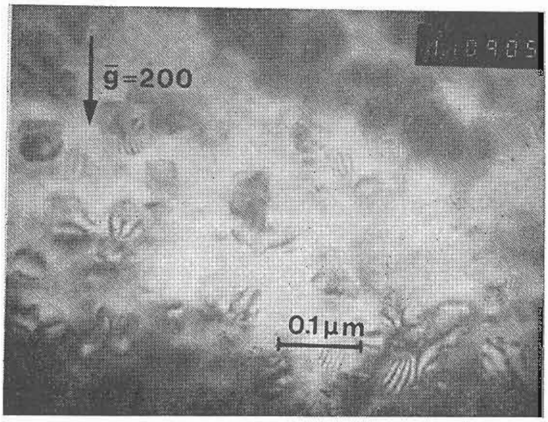

Fig. 5. An area with high density of rectangular defects. Some of the rectangles show distorted Moirè fringes revealing not only rotation but also a change of the lattice parameters in these regions.

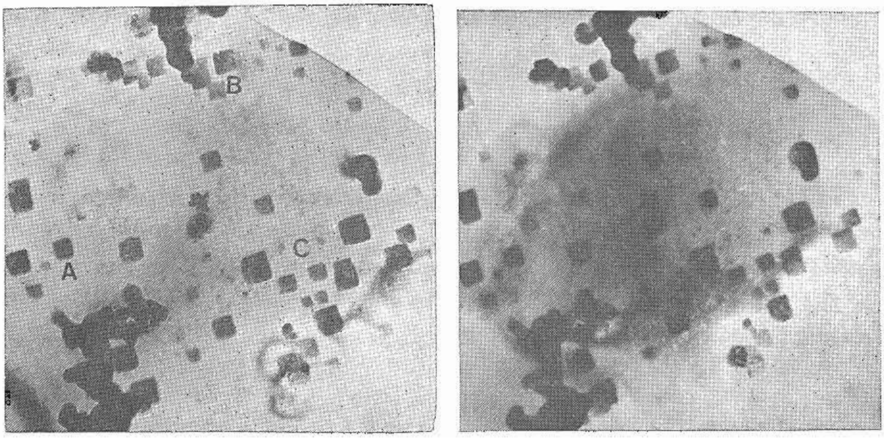

Fig. 6. Stereo-photograph, angle of tilt ± 7°.

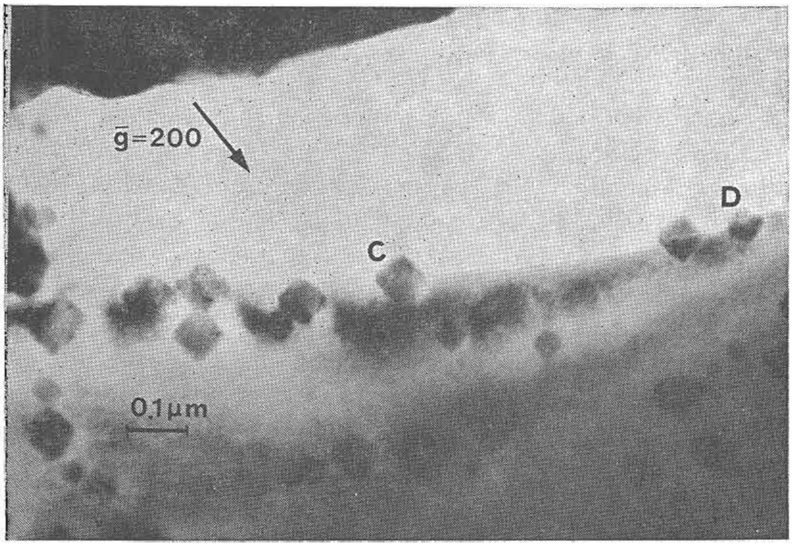

Fig. 7. In the areas C and D rotation Moirè patterns are visible only in the overlapping part of the rectangles with the matrix.

around these defect regions and according to Ashby and Brown [10] a black-white contrast should appear. No such contrast has been observed around the rectangles. The different chemical behaviour combined with the same lattice parameter could be explained by stoichiometric variation of the rectangular area compared to the matrix. Thus, large areas of the crystal should be considered as mosaic with a deviation from stoichiometry.

Specimens that have been prepared only by Argon ion bombardment etching, showed small spots about 50 ~ 100 Å in size. The contrast of the spots change in a regular manner across the thickness extinction contour bands (Fig. 8). Spots exhibitiug such a change in contrast correspond to defected regions where the structure factor is smaller than that of surrounding perfect regions.

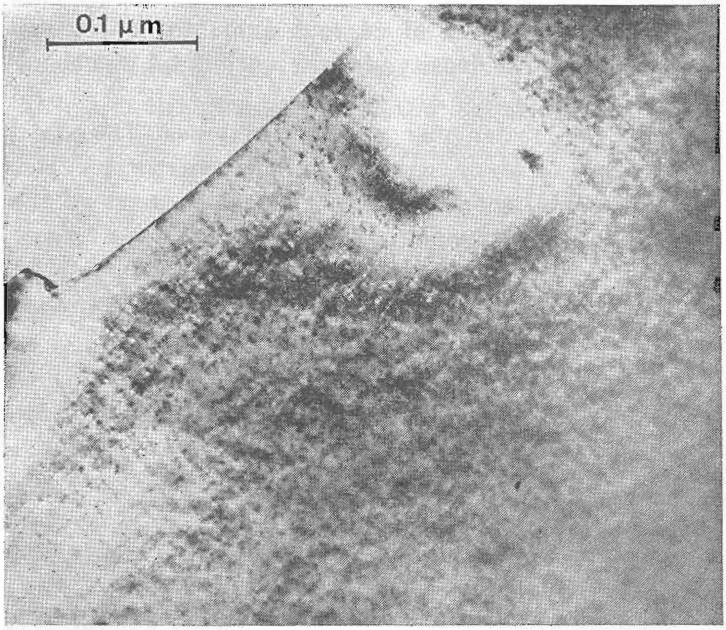

Fig. 8. Rotatiou damages produced after specimen preparation with ion bombardment 5 keV Ar ions. Overating reflection g = *200.*

The density of these spots is about $2 \times 10^7 cm^{-2}$ for a region of about 1500 Å in thickness.

The same defects could be produced in specimens which have been prepared only by chemical polishing after a loug observation in the electron microscope. Since a 100keV electron beam can not transfer sufficient energy to cause a displacement of the atoms in the Cu_2O, the creation of the defects is probably due to radiolysis [8]. Fig. 3(b) was taken under the same diffraction condition as Fig. 3(a) after a sequence of tilting experiments, the damages are evident.

4. CONCLUSIONS

In cuprous oxide single crystals grown by the grain growth method the matrix has a low density of normal dislocations. Additional dislocation loops, produced by the prismatic punching mechanism, have also been observed as a result of the crystal quenching from a temperature near the melting point. It was not possible to identify the precipitates that produce these loops, but it is probable to be related with the eutectoid decomposition of cuprous oxide to copper and cupric oxide during cooling. The density of these precipitates was about $10^6 cm^{-2}$ and the average radius 300 Å.

There are also rectangular misoriented areas. The size of these areas is too small to be observed by optical microscope. The density of the rectangles was about $10^8 cm^{-2}$. Thus, large areas of the crystal should be considered as having a mosaic structure. All these defects can influence the semiconducting properties of the material and it is certain that if we reduce all these faults, we would improve the electrical properties of the material considerably.

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ΠΕΡΙΛΗΨΗ

ΣΦΑΛΜΑΤΑ ΣΕ ΜΟΝΟΚΡΥΣΤΑΛΛΟΥΣ GuO

Ὑπὸ
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Μονοκρύσταλλοι ὑποξειδίου τοῦ χαλκοῦ (Cu_2O) παρασκευάστηκαν μὲ τὴ μέθοδο «grain growth». Οἱ κρύσταλλοι παρουσιάζουν μικρὴ συγκέντρωση ἐξαρμόσεων μὲ διανύσματα Burger α < 110 > καὶ α< 100 >. Παρατηρήθηκαν ὅμως κυκλικὲς ἐξαρμόσεις, οἱ ὁποῖες σχηματίστηκαν κατὰ τὴν ταχεία ψύξη τῶν κρυστάλλων ποὺ ἀποτελεῖ τὴν τελικὴ φάση τῆς παρασκευῆς. Ἐπίσης παρατηρήθηκαν τετραγωνικὲς περιοχές, οἱ ὁποῖες παρουσίαζαν κροσσοὺς Moirè, ποὺ ὀφείλονταν σὲ μιὰ ἐλαφρὰ στροφὴ τοῦ πλέγματος τῶν περιοχῶν αὐτῶν σὲ σχέση μὲ τὸ πλέγμα τοῦ ὑπόλοιπου κρυστάλλου. Ἐξαιτίας τοῦ γεγονότος αὐτοῦ μποροῦμε νὰ χαρακτηρίσουμε τὰ τμήματα αὐτὰ τοῦ κρυστάλλου ὅτι ἐμφανίζουν μωσαϊκὴ ὑφή.