

## Microstructure of Thin Single Crystals of Copper\*

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Single-crystal films of copper of 700–800 Å thickness have been prepared showing high densities of wide stacking faults. Variations in the annealing treatment of the films affect the nature of the imperfections occurring in the film.

THE study of single crystals of copper between 700 and 800 Å in thickness was undertaken in connection with the investigation of the oxidation of copper crystals at moderate temperatures. Harris, Ball, and Gwathmey<sup>1</sup> had observed interesting variations in the textures of oxide films removed from various faces of copper crystals of about 1-cm thickness. By oxidizing thin copper crystals we hoped to make electron microscopic observations of the cuprous oxide nuclei in place on the metal and thereby detect any influence of imperfections in the structure of the substrate on the nucleation and growth of the oxide. The method used in preparing the thin film has led to a higher density of stacking faults than previously observed in copper, and this report concerns some details of the preparation and the resulting microstructure of the copper as observed in electron micrographs and diffraction patterns.

### PREPARATION OF COPPER FILMS

The films were prepared by condensation of copper onto heated NaCl crystals with subsequent treatment adapted from the procedures used on massive crystals.<sup>1</sup> The evaporation and condensation was carried out under a bell jar at a residual pressure of about  $10^{-5}$  mm Hg. The copper (99.999%) was condensed at a rate of

about 400 Å/min for two minutes. The NaCl surfaces were prepared by polishing cleavage faces on moist metallographic polishing cloth or paper followed by quick rinses in water and methanol; this treatment gave a lower density of steps on the surface as revealed by decoration with gold than appeared on unpolished cleavage faces. Two crystals were mounted in a heated support (Fig. 1) which surrounded the crystals except for windows (6×22 mm) for admission of the condensing metal. The crystals were maintained at 330°C during the condensation and then cooled to room temperature in 7 or 8 min.

The condensed film was annealed in a stream of hydrogen either before or after stripping from the NaCl substrate. In the former case the film on the substrate was transferred to a glass vacuum line and heated in purified hydrogen at one atmosphere to 630°C for ten minutes or longer. After cooling in hydrogen, the film was floated off on water and segments were picked up on electron microscope specimen grids. The mounted films were heated to 420°C in hydrogen for ten minutes, a treatment sufficient to reduce the oxide formed during the 15-sec contact with water. In the other procedure the freshly condensed film was stripped and mounted on specimen grids and then annealed in hydrogen at

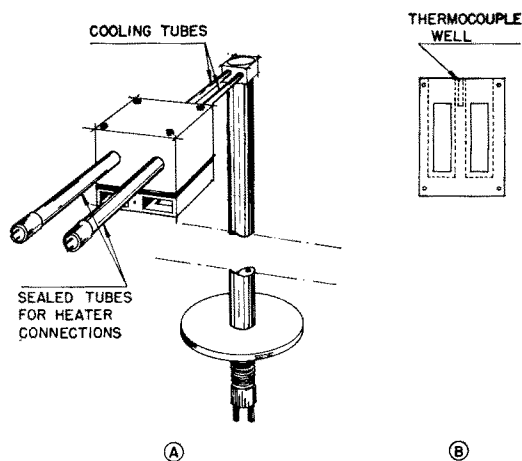


FIG. 1. (A) Heater support for NaCl substrates. (B) Bottom view of heater block showing thermocouple well and two channels for NaCl crystals.

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<sup>1</sup> W. W. Harris, F. L. Ball, and A. T. Gwathmey, *Acta Met.* 5, 574 (1957).

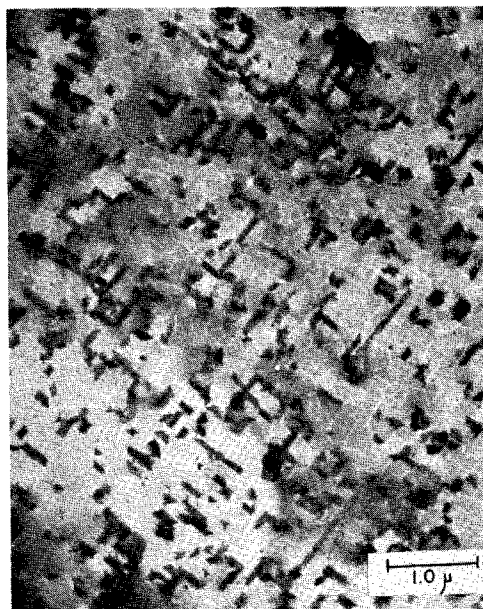


FIG. 2. Electron micrograph of unannealed copper film.

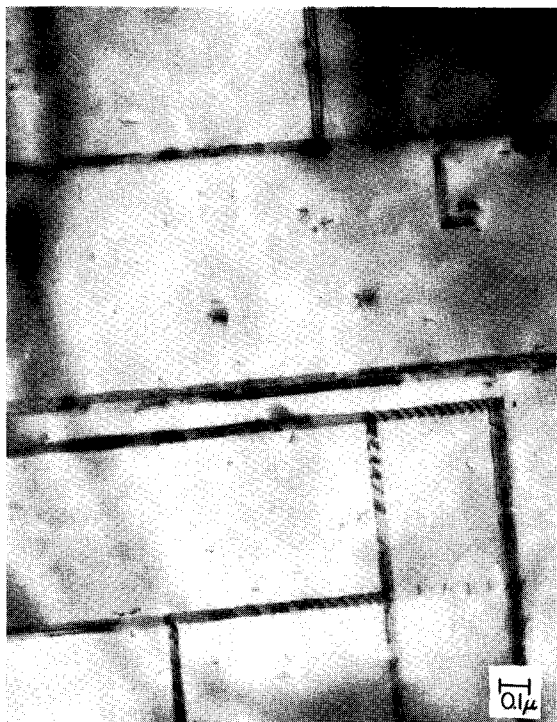


FIG. 3. Electron micrograph of copper film annealed on NaCl substrate. The distinguishable regions of Fig. 2 have coalesced, and numerous dislocations and stacking faults are present.

630°C. Several other variations were tried in some of the stages of the preparation (including the pretreatment of the NaCl surface and the use of helium or a vacuum in the annealing stage) but none of them had an appreciable influence on the copper film.

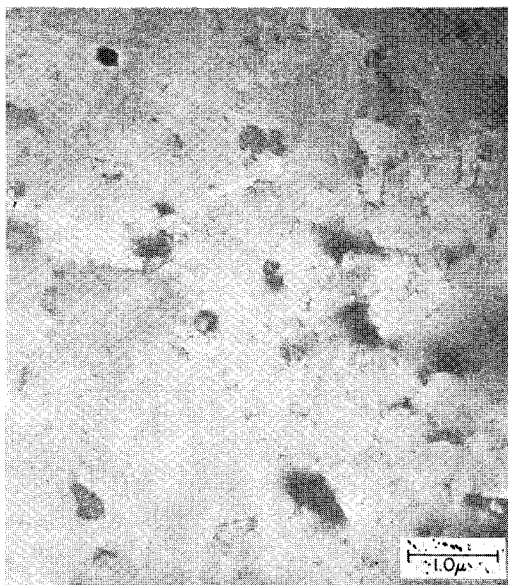


FIG. 4. Electron micrograph of copper film annealed on specimen grid. Stacking faults are absent, and the dislocation density is much higher than in Fig. 3.

#### MICROSTRUCTURE OF COPPER FILMS

The electron micrographs of Figs. 2, 3, and 4 are typical, respectively, of unannealed films, films annealed on NaCl, and films annealed after removal from the NaCl. Films from all three of these treatments give diffraction patterns similar to Fig. 5 except that the unannealed film often gives a pattern showing faint additional spots which indicate the occurrence of (111) twins. These disappear with either type of annealing and the crystalline copper has a uniform alignment over the whole area of the films.

In the micrographs the unannealed films show uneven textures (sometimes including holes) depending on the condensation rate and temperature; grains of 1000-Å diameter separated by thinner stripes of copper but having a common orientation are usual. In addition, some films with larger grains show the bands indicating

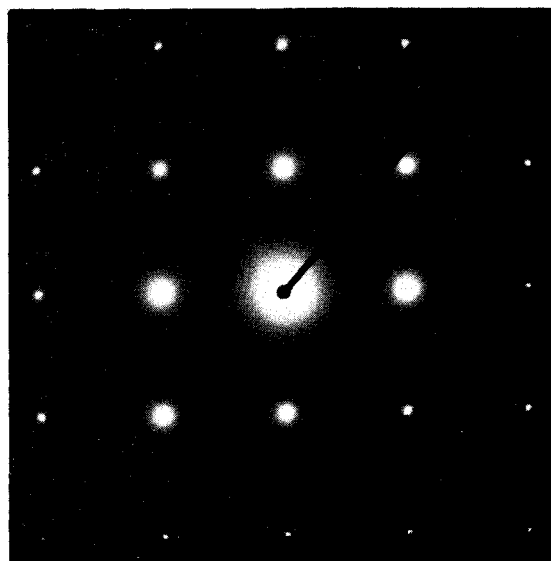


FIG. 5. Electron diffraction pattern of copper single-crystal film.

stacking faults which may extend across two or three grains, although the width of the faults is usually less.

The annealed films are more continuous without any of the small islands showing in the unannealed films. Annealing on NaCl results in many stacking faults with widths reaching  $2\mu$  or more and with faulted areas amounting to  $5 \times 10^4$  sq cm per cubic cm of films. The film in Fig. 3 shows interesting details which sometimes appear in the stacking faults. By contrast the films annealed after removal from the NaCl show only occasional narrow stacking faults but a high average density of dislocations amounting to  $10^9$  per sq cm.

The stacking faults of high density and  $2.0\text{-}\mu$  widths produced by the annealing on NaCl is a new result for copper, although faults of the  $0.1\text{-}\mu$  width shown here in

the unannealed films have been previously observed by Votava and Fourdeux.<sup>2</sup> A high density of wide faults is ordinarily associated with low stacking-fault energies and the present observations favor a lower value such as the 40 ergs/cm<sup>2</sup> proposed by Thornton and Hirsch<sup>3</sup> or about 20 ergs/cm<sup>2</sup> suggested by Inman and Khan<sup>4</sup>

<sup>2</sup> E. Votava and A. Fourdeux, Proc. Intern. Conf. Electron Microscopy, 4th, Berlin, 1958 1, 556 (1960).

<sup>3</sup> P. R. Thornton and P. B. Hirsch, Phil. Mag. 3, 738 (1958).

<sup>4</sup> M. C. Inman and A. R. Khan, Phil. Mag. 6, 937 (1961).

rather than the value of 170 ergs/cm<sup>2</sup> reported by Seeger, Berner, and Wolf.<sup>5</sup>

The possibility of influencing the density of dislocations and of stacking faults by variations in the annealing treatment is being applied to studies of the effect of imperfections in the copper film on the nucleation, epitaxy, and growth of cuprous oxide formed during treatment with oxygen. The results of the oxidation studies will be published elsewhere.

<sup>5</sup> A. Seeger, R. Berner, and H. Wolf, Z. Physik 155, 247 (1959)

## Interpretation of the Neutron or X-Ray Scattering from a Liquid-Like Binary\*

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In the general liquid-like binary three radial densities relating to  $A-A$ ,  $B-B$ , and  $A-B$  pairs are needed to characterize the scattering. The three densities can be obtained by the Fourier inversion of the weighted combination of three diffraction patterns, each of which differs by the alteration of the scattering of one or both components. If the density of atoms regardless of type is the same around both components, then only two functions, one this distribution, and the other involving the order between  $A-B$  pairs is needed to characterize the scattering. This case is the liquid analog of the crystalline alloy with short-range order. These two functions can be obtained by the Fourier inversion of a weighted combination of two patterns differing by the alteration of the scattering of the components.

### INTRODUCTION

ONE method of interpreting the scattering from a liquid-like binary which has been highly successful depends on there being a clearly defined molecular unit. The molecular model<sup>1</sup> is varied until agreement is achieved, and a refinement allows for intramolecular interferences. This method fails in the absence of a molecular unit. The second method which applies to this more general liquid-like binary has been considered by Warren and his fellow workers.<sup>2</sup> By assuming the same angular dependence for the atom scattering factors, they succeeded in inverting the scattering from vitreous silica and analyzing the resulting distribution curve in terms of prominent interatomic distances. The problem is that correlations between atom types are not recognizable either as specific interferences in the scattering or as unambiguous peaks in a transform, so that additional clues are helpful if not necessary.

Warren<sup>3</sup> has suggested an improvement based on the qualitative comparison of x-ray and neutron data.

However, with straight-forward application of neutron and x-ray or electron diffraction, isomorphous replacement, or isotopic enrichment this ambiguity can be eliminated as has been pointed out by Vineyard.<sup>4</sup> The objectives of this paper are to demonstrate the three radial densities required to describe the scattering from the most general liquid-like binary, to give the condition under which this number is reduced to two, and to give the combinations of diffraction patterns necessary for the unique determination of these densities or quantities derived from them.

### THEORY

Consider the (elastic) scattering of x rays, electrons, or neutrons from a system of  $N$  atoms of two species  $A$  and  $B$ . Express the scattering of x rays in electron units, of neutrons in units of the scattering from a nucleus of radius  $10^{-12}$  cm, and of the electrons in units

\* Work supported by the U. S. Atomic Energy Commission.

<sup>1</sup> See, for instance, R. W. James, *The Optical Principles of the Diffraction of X-rays* (G. E. Bell & Sons, London, 1950), Chap. IX; M. B. Pirene, *The Diffraction of X-rays and Electrons by Free Molecules* (Cambridge University Press, London, 1946), Chap. VII.

<sup>2</sup> B. E. Warren, H. Krutter, and O. Morningstar, J. Am. Ceram. Soc. 19, 202 (1936).

<sup>3</sup> B. E. Warren, paper presented at the Gordon Research Conference on Physical Metallurgy, 25-29 June 1962, Meriden, New Hampshire.

<sup>4</sup> G. H. Vineyard, *Liquid Metals and Solidification* (American Society for Metals, Cleveland, Ohio, 1958), pp. 1-48.