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Formation of Stacking Faults in Single-Crystal Films of Copper Grown on NaCl, KCl, and LiF Substrates

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Copper films 700 Å thick deposited on NaCl or KCl at 330°C are preferentially oriented on the (001) plane, and after heating at 630°C they exhibit complex stacking faults of 2 to 3 μ in width. Examination of carbon replicas and of platinum-shadowed copper films shows that straight surface terraces of 50 to 100 Å in elevation occur over the faults and that these terraces are formed in the copper film while on the substrate. Copper deposited on cleaved LiF substrates shows several orientations, and annealing up to 745°C produces no preferential growth among them; no stacking faults appear in the annealed film. On the LiF preheated above 700°C before cleaving, copper films are deposited as single crystals and when annealed at 745°C show complex stacking faults and terraces as observed with the chloride substrates. In all cases the faults are believed to form under compressive stresses in the single crystal of copper as the film on the substrate is cooled from a high temperature.

INTRODUCTION

ELECTRON micrographs of thin (700–800 Å) copper films prepared by condensation at 400 Å per minute onto (001) sodium chloride substrates at 330°C have previously[1] shown short twin boundaries and an uneven texture; their diffraction patterns indicate single crystals with some twinning. When these films are subsequently heated in 1 atm of hydrogen to 630°C with the copper film still in place on the substrate the micrographs then show wide complex stacking faults (up to 2 μ wide with 5×10^4 cm^2 of faulted area per cm^3 of copper) and dislocation densities of 10^7 cm^{-2} (Fig. 1). By contrast the films which are heated in hydrogen to 630°C only after removal from the substrate contain no stacking faults but have a hundredfold higher density of dislocations (Fig. 2). Since this high density of wide stacking faults in the substrate-annealed films represents a new observation in copper, the study has been continued in the hope of identifying the factors which are responsible for the formation of the stacking faults.

The observation of faulting only in films that are heated on the substrate and then floated off on water and picked up on specimen grids suggests that the formation of faults is due either to an interaction with the substrate during the heating or to stresses applied during the stripping and mounting process. Accordingly the surfaces of the NaCl substrate and of the deposited copper have been examined with the aid of carbon replicas at all stages of the film preparation, two other substrate materials have been used, and the stripping process has been varied to test its influence on fault formation.

REPLICAS OF THE NaCl SUBSTRATE AND COPPER SURFACES

The NaCl substrate has been used both freshly cleaved and after polishing on 4/0 emery paper followed by rinsing for a few seconds at room temperature in streams of water, dry methanol, and dry air. Some preference was felt for these polished surfaces because under decoration by gold[2] they showed larger smooth areas than the cleaved surfaces. Platinum-shadowed carbon replicas of both types of surfaces did not show any roughness coarser than the grain of the replica material, nor did any differences appear in the copper films grown on the two surfaces.

When the NaCl is heated to 330°C for several minutes under a residual pressure of about 10^{-5} Torr (the conditions during the deposition of copper) and then cooled, the carbon replica shows that an appreciable thermal etching occurred, with many small irregular bumps up to 0.1 μ in length and heights up to 50 Å;

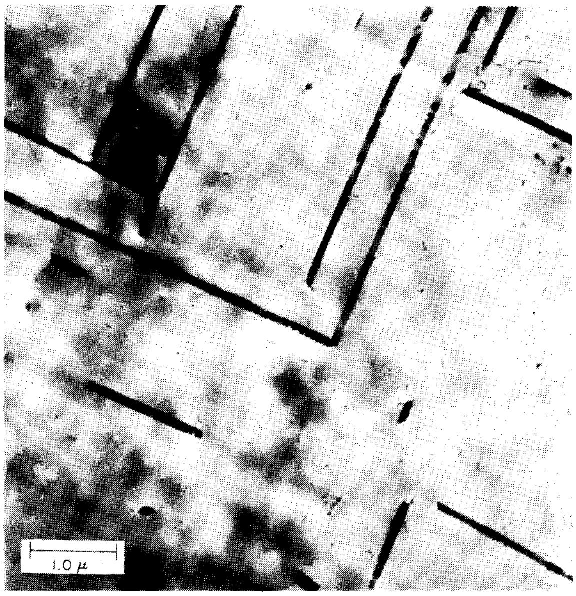

FIG. 1. Micrograph of Cu film heated at 630°C on NaCl. ×11 400. The complex stacking-fault images combined with isolated dislocations are characteristic of this film treatment.

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[1] L. O. Brockway and R. B. Marcus, J. Appl. Phys. 34, 921 (1963).

[2] G. A. Bassett, J. W. Menter, and D. W. Pashley, Proc. Roy. Soc. (London) A246, 345 (1958).

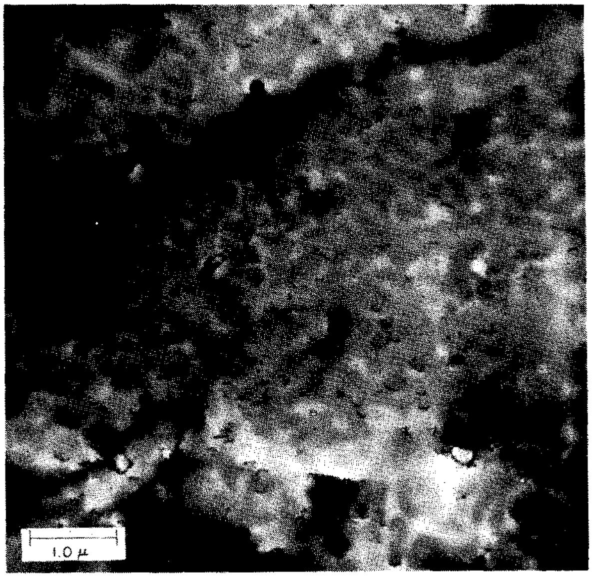

FIG. 2. Micrograph of grid-annealed Cu film from NaCl. ×11 400. The higher density of dislocations and the absence of stacking faults is characteristic.

irregularly curved long steps with heights up to 200 Å also appeared (Fig. 3). It is evident that minor variations in the roughness of the original surface are not related to the characteristics of the surface on which the copper is actually deposited.

NaCl crystals without copper were also subjected to the conditions used for annealing copper films (630°C for 10 min in 1 atm of hydrogen); replicas of the resulting surfaces show curved contours with steps about 100 Å high as well as straight-sided protrusions and pits as large as 1500 Å in height and depth (Fig. 4). The changes in elevation occurring in some areas are occasionally as great as three or four times the average thickness of the copper deposit.

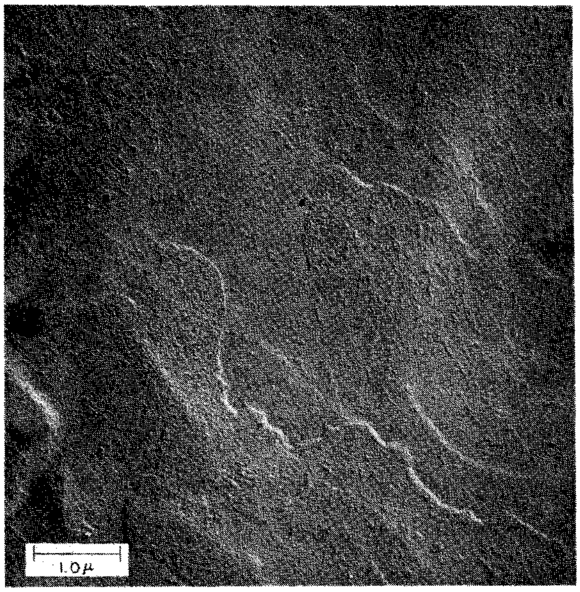

FIG. 3. Replica of NaCl heated at 330°C. ×11 400.

In copper films deposited at 330°C the direct micrographs show islands of 1000 to 1500 Å in diameter separated by channels of about 200 Å in width. Replicas of the copper surface have the appearance of crystallites with corners and edges often protruding by 50 Å above the average surface plane. After the copper is heated to 630°C on the substrate, examination of replicas shows that the surface of the copper is generally smooth with particles about 50 Å across and that two special features appear. The first is grossly rough areas with heights and depths sometimes exceeding 3000 Å (Fig. 5); the other is a rectangular array of straight terraces with changes in elevation up to 200 Å. The gross roughness usually involves no more than 1% of the total area, while the system of straight terraces is found over about half of the total area. Replicas indicate that after cooling to room temperature the copper film generally closely follows the asperities in the substrate surface. One area with deep square-cornered etch pits has the copper fitted tightly over the corners; in another area the curved 100-Å contours of the substrate show on the upper surface of the copper.

FIG. 4. Replica of NaCl heated at 630°C. ×11 400.

Replicas have also been prepared from the 630°C-annealed copper after it has been stripped from the substrate onto water, picked up on a specimen grid, and reduced in hydrogen at 420°C to remove traces of oxide formed during the contact with water. Now all the areas observed show only the rectangular array of terraces (Fig. 6) with a general background of particles of about 50 Å in diameter. Most of the terraces have elevation changes falling in the range between 50 to 150 Å; it is doubtful that heights appreciably less than 50 Å could be detected. The rough features observed in the films supported on the substrate are never found in the grid-mounted films.

Because the distribution of terraces is similar to the stacking-fault array previously observed in direct micrographs of grid-mounted films, platinum was evaporated at a 30° angle onto grid-mounted copper films in order to obtain micrographs simultaneously showing surface contours and diffraction effects from structural defects in the copper. While there is difficulty in applying enough platinum to produce shadows without obscuring the internal structural detail of the copper, several micrographs show that the fringed bands of the stacking faults coincide with shadows of the terraces, and no resolved fault patterns were seen without the shadows. Thus, the terraces on the surface do correlate in position with the stacking faults.

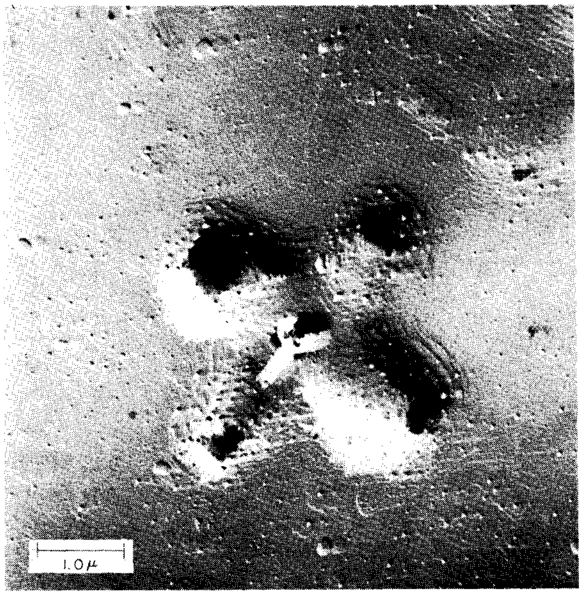

FIG. 5. Replica of Cu film heated at 630°C on NaCl. ×11 400.

Some observations on grid-mounted faulted films during reheating in a high-temperature specimen holder in the electron microscope show that some of the faults shift their positions under the influence of thermal stresses. Some of the images disappear and reform at new locations, but heating to 630°C after removal from the substrate does not eliminate the faults.

OTHER SUBSTRATES

The choice of other substrates was confined to readily available alkali halides. Of these, KCl and LiF were chosen after consideration of their coefficients of thermal expansion, vapor pressures, unit cell sizes and changes in chemical composition from NaCl. The specimens used were obtained from the Harshaw Chemical Co.

KCl. The differences in copper films grown on KCl and NaCl under the same conditions are not detectable in the micrographs of the films. The same (001) orientation of the copper film and the same rectangular array of stacking faults oriented on the (111) planes (Fig. 1) are observed in films grown and annealed on KCl; also the terraces of Fig. 6 appear in carbon replicas of these films.

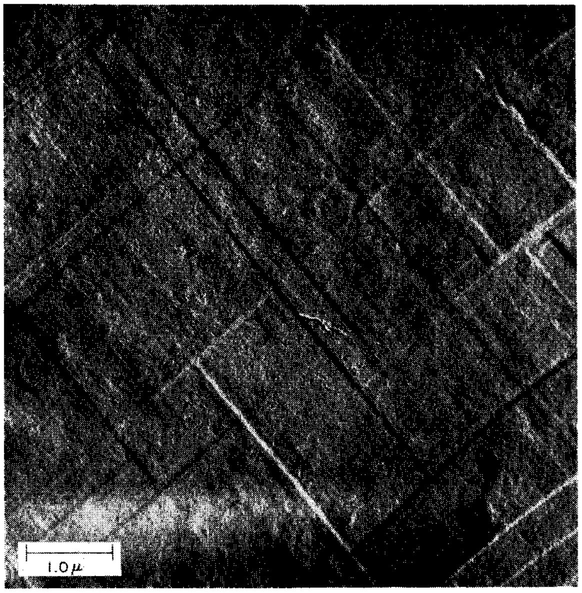

FIG. 6. Replica of Cu film heated at 630°C on NaCl and mounted on specimen grid. ×11 400.

Replicas made at intermediate stages as for the NaCl substrates show that the higher vapor pressure of KCl produces more thermal etching and the KCl surfaces are rougher than the NaCl ones, especially after heating to 630°C. The pits and bumps on the surface either with or without copper range up to 50% higher than on NaCl surfaces. The extra roughness, however, leaves no detectable difference in the stripped films.

LiF. The use of LiF showed a number of interesting differences from NaCl.

The LiF crystals were freshly cleaved or cleaved after a preliminary heating above 700°C.

Fresh cleavage surfaces of LiF are smooth enough to show no features resolved by the carbon replicas except for occasional steps of about 3000 Å. After heating to 330°C (the deposition temperature for the copper) the

TABLE I. Certain properties of the substrates and of copper.

	Lattice constant Å	Closest approach of atoms in (001) plane, Å	Coefficient of linear expansion, $\times 10^4$	Vapor pressure log p(Torr) 330°C	630°C	745°C
KCl	6.28	3.14	0.380	−6.25	−2.05	
NaCl	5.63	2.82	0.404	−8.85	−2.43	
LiF	4.01	2.00	0.450	−10.13	−2.82	−2.43
Cu	3.61	2.55	0.16[a]			

[a] Value measured on bulk, polycrystalline material.

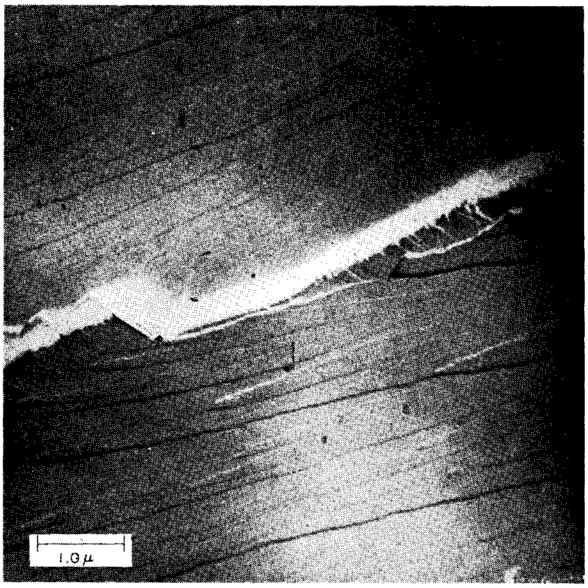

FIG. 7. Replica of cleaved LiF heated at 330°C. ×11 400.

surface shows many long terraces no more than 100 Å high and either parallel to the large cleavage steps or at an angle of 10° (Fig. 7). Copper films deposited at this temperature and then mounted for electron microscopy show an irregular texture with more thickness variation than observed in unannealed films on NaCl and often had holes extending through the film. This difference suggests a lesser mobility of copper on LiF at 330°C, and it is confirmed by the diffraction patterns which show an array of (111) and (200) reflections with some randomness around the normal to the film. No one orientation is predominant.

Annealing experiments were carried out at 630°C and 745°C. The bare substrate is not roughened as the chlorides were; the surface is quite smooth (within the 30-Å resolution of the carbon replica) with two sets of striations at 60° to each other (Fig. 8). An interesting feature is the large curved humps located along the cleavage steps: while each hump covers about $4\ \mu^2$ the total is only a small part of the area of the crystal face.

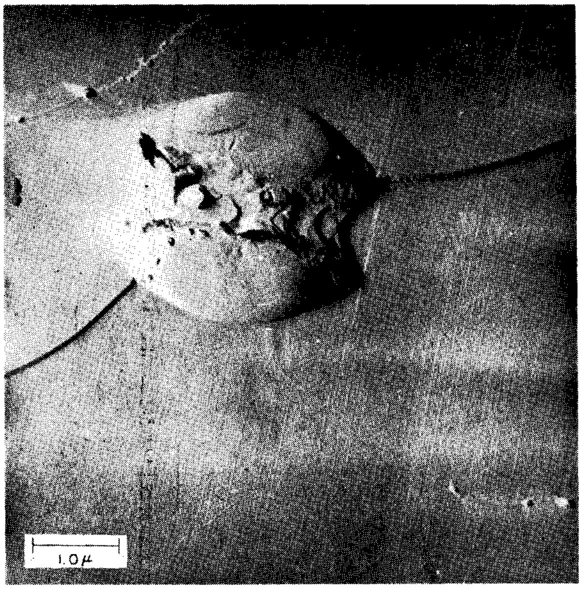

FIG. 8. Replica of cleaved LiF heated at 745°C. ×11 400.

The copper film annealed at 630°C or at 745°C on the cleaved LiF surface very rarely shows the stacking faults always observed in copper annealed on the other substrates (Fig. 9). The grain size has increased only to 2 or 3 μ; and while the number of distinct orientations is less than in the film deposited at 330°C, there is still no predominance of the (001) orientation.

The unexpected behavior of copper on LiF led to a variety of experiments, among which it was discovered that a preliminary heating of the bulk crystal to 745°C for 10–30 min prior to cleaving at room temperature resulted in a quite different behavior. The preheated crystals cleaved more readily and showed many more cleavage steps, each only a tenth as high as on the unheated crystals. Heating the cleavage faces of the preheated crystals to 330°C produced a smoothness comparable to that seen in Fig. 8, but after heating at 745°C the smooth areas are separated by many curved steps of 200 Å in height.

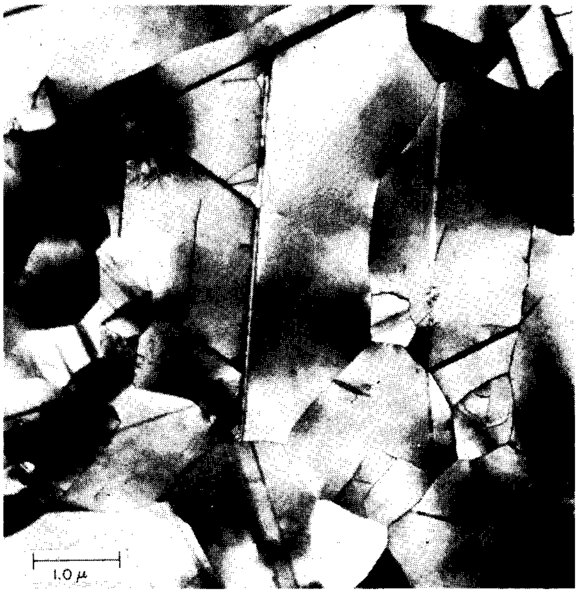

FIG. 9. Micrograph of Cu film heated at 745°C on cleaved LiF. ×11 400.

Copper deposited at 330°C on the preheated cleaved surface shows smooth regions often 3000 Å wide, but replicas taken from the surface of such films show a rectangular array of crystal corners and edges extending as much as 200 Å above the adjacent surface (Fig. 10). Annealing at 630°C produces smooth copper films showing only an occasional stacking fault of a micron in width, while annealing at 745°C produces the familiar extensive array of stacking faults observed in films from NaCl and KCl, although the stacking faults from LiF show widths up to 8 or 10 μ and occasional dislocation networks appear (Fig. 11).

Comparison of Figs. 9 and 11 shows the pronounced effect on the annealed copper film of preheating the LiF before it is cleaved. When the copper film treated as for Fig. 11 is replicated before stripping from the substrate, most of the area of the upper surface shows straight terraces up to 200 Å high similar to those of the grid-mounted films annealed on NaCl as shown in Fig. 6.

Thus there are four major differences observed between the properties of the freshly cleaved LiF and those of crystals which had been preheated above 700°C before cleaving. (1) The preheated crystals cleaved more readily. (2) Their cleavage surfaces were smoother in the sense that the maximum cleavage steps were only a tenth as high as the 3000-Å steps regularly occurring on the unpreheated cleaved crystals. (3) The surfaces from preheated crystals released the deposited copper films more easily, although still requiring hydrofluoric acid in the water on which the film was floated. (4) The crystallographic orientation of the copper deposited on the surfaces from preheated crystals lies with the (001) plane parallel to the substrate, and the films annealed at 745°C show the many wide stacking faults and the associated surface terraces observed from NaCl surfaces. The films on the surfaces from unpreheated LiF are irregular in orientation both after deposition and after annealing, and no stacking faults appear.

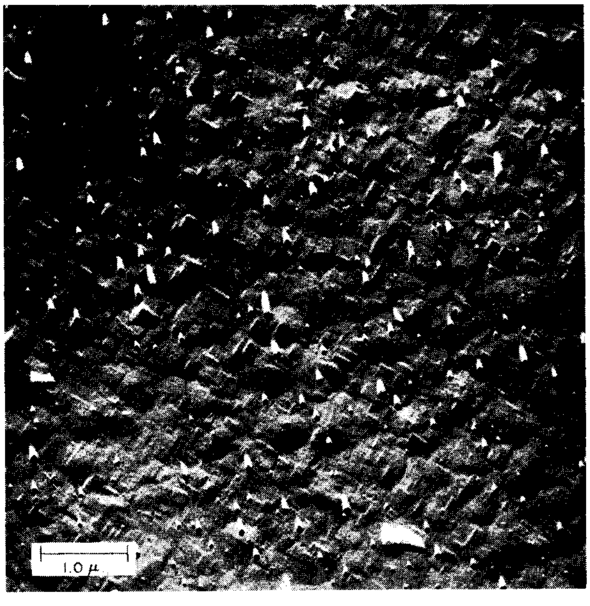

FIG. 10. Replica of Cu film deposited at 330°C on preheated LiF. ×11 400.

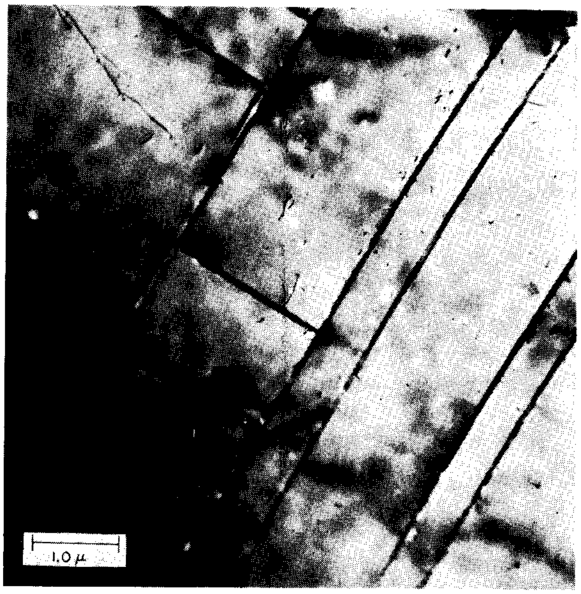

FIG. 11. Micrograph of Cu film heated at 745°C on preheated LiF. ×11 400.

TEST OF THE STRIPPING PROCESS

The removal of copper films from the crystalline substrates is accomplished by holding the upper surface of the crystal at an angle of 30° to a water surface which is slowly raised. The leading edge of a film on a NaCl or KCl crystal is released immediately; and as the crystal is immersed, the bend in the film moves along until the last edge is released and the film floats free. In the case of LiF substrates hydrofluoric acid is added to the water to a concentration of 8% and even then the total release of the film requires 10–15 min. In all cases the film is subjected to a bending stress until it floats on the water, where the surface tension serves to keep the film unwrinkled.

In early observations on the films from NaCl it was suspected that the stresses applied in the stripping process might contribute to the properties of the film as observed in the microscope after mounting on the specimen grids. Accordingly, some experiments were conducted in which the film was mechanically supported with a layer of paraffin wax or carbon during the stripping process.

When a layer of paraffin wax of about 1-mm thickness was applied to the annealed copper film still on the NaCl substrate, the subsequent immersion in water caused the paraffin to break away in rigid blocks of a few square mm in area with the copper adhering to the paraffin. No bending of the copper and paraffin was observed. The specimens were then mounted on grids and the paraffin leached away with benzene. Electron micrographs of the resulting films again showed the familiar stacking-fault patterns.

It is believed that the support during stripping afforded by the paraffin was sufficient to substantially reduce the bending and stretching stresses accompanying the usual stripping process. The observation of stacking faults in these supported films leads us to conclude therefore that the stresses during stripping are not significant in producing stacking faults.

DISCUSSION

The texture and structure of copper films at various stages in their preparation and mounting can now be described. The cleaved NaCl substrate as presented to the condensing copper vapor has many curved steps of 100 to 200 Å in height. The 700-Å-thick copper film condenses into 1000 to 1500-Å islands separated by thinner channels of about 200 Å in width. The islands are single crystals with their cubic axes oriented parallel to those of the substrate, so that the whole film gives a single crystal diffraction pattern except for weak twin spots and with some twin boundaries or short stacking faults showing in the micrographs. After heating to 630°C the films on the substrate show occasional grossly rough features (3000 Å high) with the intervening smooth areas crossed by straight terraces of 50 to 150 Å in height and lying in the (110) directions on the surface. These films after mounting for electron transmission show only the straight terraces on the surface and these correlate with the wide stacking faults appearing in the micrographs.

The stacking-fault images in the micrographs are complex. Some parts show a simple fringed pattern with either three or four parallel fringes extending from 2000 to 3000 Å along the image. Most of the images show many discontinuities cutting across the fringes at irregular intervals of a few hundred angstroms.

In the first type of image the system of parallel fringes may be interpreted by the kinematic theory[3] of diffraction contrast in electron microscope images of structural defects as indicating a uniform thickness of the copper film with variations less than about 100 Å. The gradual transitions from three to four fringes occasionally observed are due to an increase of thickness exceeding 100 Å but less than 200 Å; such transitions occur over a distance of about 1000 Å along the stacking fault. The various discontinuities observed cannot usually be interpreted in detail, but they indicate stacking faults involving displacements along more than a single plane of atoms. Within a range of as many as a hundred successive layers of atoms, displacements seem to occur between groups of atom layers, each group having only a few layers in it. Sometimes in passing along the faulted plane between an adjacent pair of groups the displacement disappears rather abruptly and the pair of groups has resolved itself into a single group of atomic layers having the correct single-crystal stacking within the group. The complication of having successive stacking faults separated by only a few atom layers has an effect where the faulted planes reach the surface of the crystal. For a single faulted plane the terrace at the surface need be no more than a fraction of an atomic diameter in height, but the complex of faults occurring in these films gives rise to the surface terraces with over-all heights ranging from 50 to 150 Å. The details of contours in the elevation of a terrace are not resolved in the micrographs of the carbon replicas, but it seems probable that each terrace involves a series of steps.

It is now apparent that the wide complicated stacking faults observed here in copper films are formed during the stage of heating the film on the substrate to 630°C and cooling again to room temperature. The terraces which correlate with the stacking faults observed directly in the films mounted for transmission are formed while the film is still on the substrate. The heating and cooling with the film in contact with the substrate is essential for the formation of the faults, but neither the presence of hydrogen gas during the heating nor the stresses applied during the stripping and mounting of the film are required for their formation.

At the high temperature the copper has a greater mobility on the substrate than it has at 330°C as shown by the increased smoothness in the general background of the micrographs. At some point during the cooling the mobility has decreased sufficiently that the copper adheres to the substrate, and because of the more than twofold greater linear contraction of the substrate the copper film is under compression at room temperature. It is now believed that the stresses applied by this compression are not wholly accommodated by elastic strains in the copper and that these stresses are responsible for slip on the (111) planes and the formation of the faults.

The influence of changing substrates would depend on the changes in forces binding the copper to the substrate and in the temperature dependence of the mobility of copper on the substrate. Neither of these factors for KCl is sufficiently different from NaCl to make an appreciable difference in the properties of copper films prepared under the same conditions on the two substrates. In the case of LiF the behavior depends very markedly on whether the crystals were or were not preheated shortly before cleaving. On the surfaces cleaved from crystals without preheating, the adhesion of copper is probably greater and the mobility at both 330°C and 630°C is certainly less as shown by the smaller grains than on NaCl at both temperatures and by the failure to crystallize in a single orientation at either temperature. The lack of wide stacking faults in films heated as high as 745°C is due in part to the failure to form large crystals of copper with (001) orientation, but the rarity of their occurrence even in small (001) crystals may be blamed on the adhesion of copper to the substrate. Preheating before cleaving produces a very different surface: the adhesion of copper is less as shown by the easier stripping in dilute hydrofluoric acid and the mobility is greater as shown by the annealing results. Indeed the balance between mobility and adhesion is

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[3] P. Hirsch, A. Howie, and M. J. Whelan, Phil. Trans. Roy. Soc. (London) **A252**, 4999 (1960).

now such that when the films are cooled from 745°C the wide stacking faults and high surface terraces are produced.

We conclude that the conditions required for the formation of wide complex stacking faults in copper films are that the film as deposited on the crystalline substrate have a nearly uniform (001) orientation, that the subsequent heating on the substrate be to a temperature high enough to afford high mobility of the copper and annealing to produce large (several microns) smooth areas, and that the cooling process involve a differential contraction of the substrate and adhering copper whereby the latter is compressed enough to cause extensive slip on the (111) stacking planes.

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Plasma Diagnostics using Lasers: Relations between Scattered Spectrum and Electron-Velocity Distribution*

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Laser light scattered from plasma electrons can be used to determine the electron density and velocity distribution. The process is classical Thomson scattering, and the scattered spectrum is constructed of the Doppler shifts of the electrons. The spectrum $I(\mathbf{k})$, which appears at all angles and over a range of wavenumbers, is uniquely related to the electron velocity distribution $f(\mathbf{v})$. Either can be obtained from the other, and we derive the expressions $I(\mathbf{k})=Lf(\mathbf{v})$ and $f(\mathbf{v})=L^{-1}I(\mathbf{k})$ relativistically correctly. We also discuss the amount of information about $f(\mathbf{v})$ obtainable from a simple measurement of the scattered spectrum. The electron density and mean speed can be measured easily; more subtle features depend upon accurate observation of the low-intensity wings of the spectrum.

I. INTRODUCTION

ELECTROMAGNETIC radiation is scattered from charged particles via the classical Thomson mechanism. Monochromatic radiation scattered from a collection of freely moving charges will be spread in wavelength because of their Doppler shifts. From such thoughts springs the concept of plasma diagnostics by use of laser beams. In that art a plane-polarized beam of intensity $I_0(\mathbf{k}_0)$ is shone upon some part of the plasma. Here k_0 is the magnitude of the incident wave vector, and $\mathbf{k}_0$ includes two angular coordinates. The beam is scattered by charged particles (let us say electrons) with a spread in velocity described by a distribution function $f(\mathbf{v})$. The Thomson-scattered radiation appears at all angles, spread in wavenumber. Since, for any given incident beam, the velocity distribution uniquely determines the scattered radiation, we can write

$$I(\mathbf{k})=Lf(\mathbf{v}). \tag{1}$$

In Sec. II of this paper, we calculate the form of L, relativistically correct, in cases where plasma cooperative effects (to be described below) are absent.

This is all very well, but the real plasma diagnostics problem is the determination of $f(\mathbf{v})$. Thus we ask whether it is possible to invert Eq. (1), an operation somewhat analogous to performing an Abel inversion. That is, does a unique inverse operator

$$f(\mathbf{v})=L^{-1}I(\mathbf{k}) \tag{2}$$

exist and can it be derived? We answer affirmatively and display the result explicitly in Sec. III, relativistically correct.

Not unexpectedly, the detailed form of Eq. (2) turns out to be very cumbersome, hence of very limited immediate use to us as it stands. In Sec. IV we present some simple calculations of $I(\mathbf{k})$ for various $f(\mathbf{v})$ to illustrate the utility and difficulty envisaged in use of this technique for finding the distribution function.

II. FROM THE DISTRIBUTION FUNCTION TO THE SPECTRAL INTENSITY

Plane-polarized waves with wave vector $\mathbf{k}_0$ when scattered by individual electrons (we neglect the massive ions) may or may not add coherently. If the change in wavenumber $\mathbf{\Delta k}\equiv\mathbf{k}-\mathbf{k}_0$ corresponds to a fluctuation present in the plasma, the phases are important: We must add fields, not powers. These co-

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