FORMATION OF ETCH PITS ON COPPER SINGLE CRYSTAL PLANES

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Galvanostatic dissolution of copper single crystal (100), (110) and (111) planes in 0.1N sulphuric acid produced characterstic etch pits. On increasing the current density from 0.5 to 5mA/cm², ridges on the (110) planes, layers, spirals and square pyramidal pits on the (100) plane and layers and triangular pyramidal pits on the (111) plane are noticed. The shapes of etch pits are found to be current density dependent. The machanism of formation of etch pits is discussed.

Electrochemical etching is an important process to reveal the orientation of the substrate surface. Attempts have been made[1] to elucidate the role of defects on the anodic etching of copper single crystal planes. Several etchants which cause the development of etch pits at points where dislocations intersect the surface of copper crystals have been developed[2—5]. Successful and reproducible methods for forming etch pits at dislocations by the application of external potential have also been reported[1,6]. Mostly strong solutions of corrosive acids and oxidising agents have been used as etchants. In the present communication, the anodic etching of copper single crystal planes in dilute sulphuric acid and the mechanism of etch pits formation are given.

EXPERIMENTAL METHOD

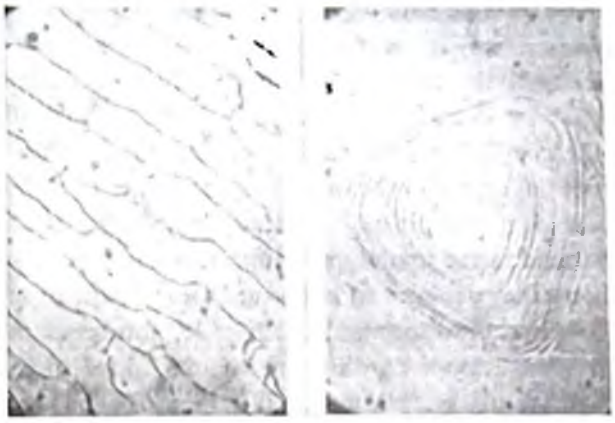
Single crystals of copper with dislocation density of 10^5/cm² were grown in specified orientation at the Oak Ridge National Laboratory, Tennessee, USA. The copper single crystals were fixed in Tygon tubing such that only the desired plane was exposed. The surface preparation prior to the anodic etching was exactly similar to that of Jacquet[7]. Anodic etching of copper single crystal planes was carried out galvanostatically in stirred, deaerated 0.1N sulphuric acid up to a was thickness equivalent to 5C/cm² (1.8μ). The dissolved surface examined under a metallurgical microscope. All microphotographs were prepared at a magnification of 600X. The experiments were repeated to ensure reproducibility.

RESULTS

Etch pits on the (111) plane

Two distinct types of etch pits are observed on the (111) plane at different current densities : (i) Layer type, and (ii) Triangular pyramidal type.

At current densities as low as 0.5mA/cm² layer-type of etch pits (Fig. 1a) in <110> direction appeared with continuous edges. As the current density was

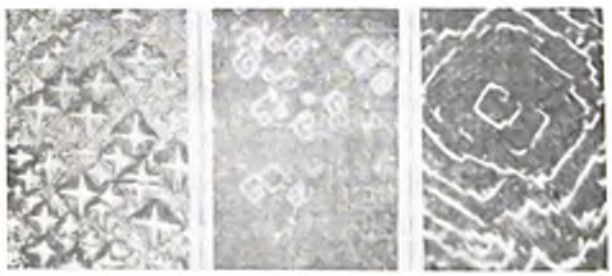


(a) (b)

Fig. 1. (a) Surface appearance of copper (111) plane after dissolution at 0.5mA/cm². (b) at 5mA/cm².

gradually increased to 2mA/cm², there were high density layer type of etch pits with still closer distance between them compared with that shown in fig. 1a. These layer type of etch pits continues to form till a current density of 4mA/cm² was reached

Triangular pyramidal pits (fig. 1b) are formed at and above 5mA/cm². Fig. 1b shows the pyramidal pits containing distinct steps with definite crystallographic



(a) (b) (c)

Fig. 2. Surface appearance of copper (100) plane dissolution at a) and b) 5mA/cm² and c) at 2mA/cm²,

direction. The base of these triangular pits are found to be aligned in <110> or <112> direction. The presence of a straight line instead of sharp point on the apex of these pyramids indicates that they are formed from a pair of screw dislocations. Here again large number of small pyramidal pits were observed at current densities above 5mA/cm². It is also found that applied current density decides the shape of etch pits.

Etch pits on the (100) plane

Pyramidal pits developed on the surface was symmetrical about (100) plane perpendicular to the surface. Typical square pyramidal pits developed, are shown in fig. 2a, observed at a c.d of 5mA/cm². Edges of these pyramidal pits were all parallel to one another in <110> direction. The frequency of pyramidal pit formation was found to be potential dependent and hence small number of big pyramidal pits appeared at low current densities and corresponding overpotentials. At high current densities and corresponding high overpotentials large number of small square pyramidal pits appeared. The apices of these pyramidal pits as illustrated in the photograph appear as sharp points but actually they are seen to be formed from a pair of screw dislocations of opposite sign. Fig. 2b illustrates many such closed loops forming pyramidal pits, giving a cubical symmetry. From this it is also evident that there should be distinct steps on the pyramids which are not seen in fig. 2a. The special feature of this photograph is that, single dislocation does not close up, but pairs of opposite ones does, resulting in the formation of a pyramidal pit.

Single dislocation is also shown to result in the formation of spiral like etch pit, typical of such are shown in fig. 2c obtained at a c.d. of 2mA/cm². However, the steps on the spiral are not so continuous in this figure as compared with the symmetry in fig. 2a. The distance between steps are lesser as it is obtained at low current densities, due to the larger radius of the nucleus for pit formation. These etch pits seem to be formed by screw dislocation operating on the surface. At specified current density range, there are special kinds of etch pits on the (100) plane of copper.

Layer type of etch pits are also observed on the same plane (cf fig. 1b) at cd < 0.5 mA/cm². They are all parallel to each other along <110> direction. Here also current density seems to decide the shape of etch pits as different kinds of etch pits are formed on the (100) plane at different current densities.

Etch pits on the (110) plane

Smooth ridges (fig. 3) appeared when (110) plane was etched at a current density of 5mA/cm². These ridges were all aligned in <100> direction. On this plane, the etch pit pattern was found to be independent of current density.

From the observed etch pits on the various planes, the shapes of etch pits seem to be dependent on orientation and current density.



Fig. 3. Surface appearance of copper (1 1 0) plane after dissolution at 2mA/cm².

DISCUSSION

Several mechanisms have been proposed to explain the surface features during crystal growth. However, one could make use of the same mechanisms to explain the topographical changes during crystal dissolution because there are sufficient evidences[8,9] supporting the reciprocity between crystal growth and dissolution.

Formation of layers on the (100) and (111) planes

Misorientation is one of the types of surface defects which results in the formation of microstep. These microsteps are active only at low current densities. During dissolution the velocity of movement of microstep depends on two factors–the proximity of microsteps to each other (ie closer the steps, the more slowly they move) and the presence of impurities (even anion of the electrolyte) Steps of the original surface do not advance at an equal rate owing to the variation in the environment. Some steps advance to catch up with other and form multisteps which are evidently made to move at a slower rate. Such process leads to accumulation of several microsteps and hence builds up a macrostep[10] (ie layers-Fig-4).

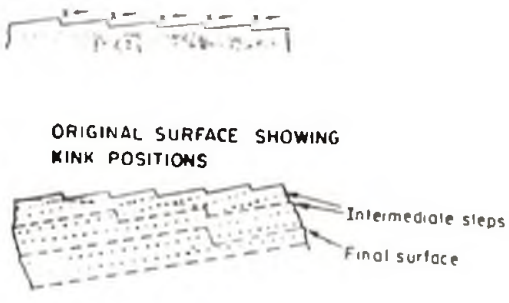


Fig. 4. Representation of the three successive stages in the formation of a macrostep by microstep bunching.

Formation of spiral on the (100) plane

Formation of spiral can be explained using screw dislocations mechanism[11,12]. If a single screw dislocation is considered to emerge on the surface with a monoatomic step on it, the step extends from a point where screw dislocation emerges to the edge of the crystal surface. Hence, the step will promote dissolution by rotating itself with one end fixed at a point where screw dislocation emerges. The resulting etch pit will take the shape of spiral (Fig. 5a).



Fig. 5a. Spiral from screw dislocation

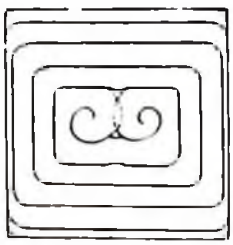


Fig. 5b. Pyramidal pit from a pair of screw dislocations of opposite sign.

Formation of pyramidal etch pits on the (100) and (111) planes

From Fig. 2b, it is evident that a pair of screw dislocations of opposite sign brings about pyramidal etch pits as similar to that observed and explained during crystal growth[13,14]. If two steps which are originating from two screw dislocations of opposite sign, are considered during dissolution, a stage is reached where two steps meet at the edge of the crystal. A 'V' shaped step is formed, the region in the 'V' being one atomic layer higher than the outside. Further removal of atoms results in increase in the angle inside the 'V'and eventually becomes a straight line (Fig 1b) going to the axis of the screw dislocations and resulting with the formation of a closed loop (Fig. 5b)

Formation of ridges on the (110) plane.

On the <110> plane, atoms can be removed in <110> and <100> directions. However, atoms can be preferentially removed in <100> direction because the <100> oriented steps are so heavily kinked that every alternative atom is a kink atom[15] (Fig. 6). The dissolution continues until the propagation of steps is slowed down and eventually blocked by the accumulated inhibiting species at the front of dissolutiod steps [9],[6]. In order sustain a given dissolution rate, the process should continue in the areas of lowest adsorption density[17]. Accordingly, the dissolution proceeds deeper into the substrate and laterally forming the grooves (ridges) and revealing {111} planes at their ends[15] (Fig. 7). The ridges shown (Fig. 7) are aligned in <100> direction and each groove is found by side faces parallel to the <100> direction.

From the observed results, it can be concluded that copper single crystals dissolve exhibiting their surface characteristics which are also shown to be current density dependent.

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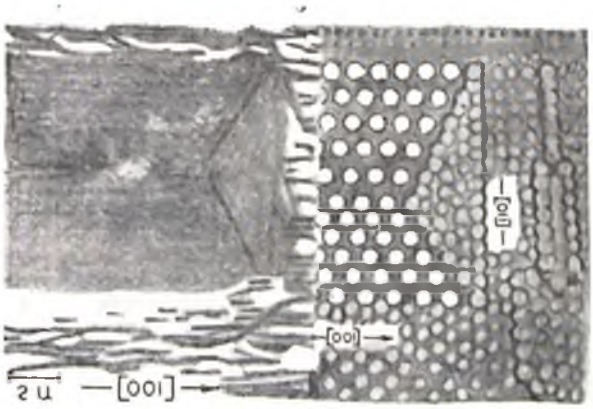


Fig. 6. Left : Part of a Groove formed on the (110) Plane
Right : The same feature is presented on a ball model

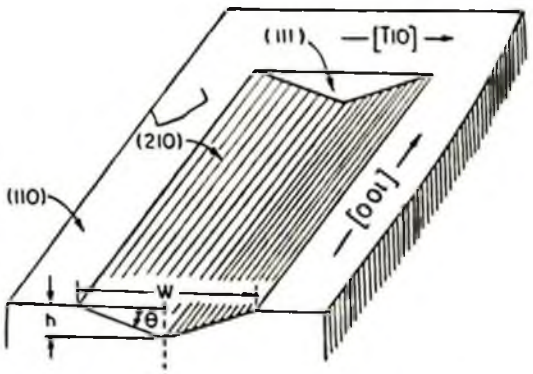


Fig. 7. Schematic presentation profile and perspective view of a Groove developed on the (110) plane

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