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Cone Formation on Metal Targets during Sputtering*

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When a Cu surface is sputtered by ion bombardment under the condition that Mo atoms arrive at the Cu surface during sputtering an unexpected phenomenon can arise: The surface of the Cu target becomes covered with microscopic cones. The cone density increases with increasing flux density of arriving Mo atoms. When the cones are closely spaced they give the target a velvet-like black appearance. The result of dense cone coverage is a lower sputtering yield and a more oblique ejection of sputtered material. The cone tops seem to consist of Mo nuclei which are constantly replenished via surface migration and protect the underlying Cu from being sputtered.

The experiments were performed in a low-pressure Hg plasma created in a discharge between a Hg pool-type cathode and an anode (dc triode operation).[1] Some exploratory experiments showed that the basic phenomenon is not different from that in an argon plasma. The plasma data were: Hg gas pressure about 1 mTorr, bombarding ion current density $\sim$1 mA/cm^2, resulting at 400 V sputtering voltage in an ion sheath thickness of about 0.2 cm. Figure 1 shows a sketch of the electrode arrangement in the sputtering section of the tube. The purpose of the shield is to achieve a gradient in the arrival rate of Mo atoms at the Cu surface. In zone A only gas scattered Mo atoms can reach the Cu surface. Zone D is in full line of sight of the Mo target and receives the full flux of Mo atoms. Zone B and C are the transition zones.

Some typical electron scanning micrographs of the Cu surface after several hours of sputtering with 400 to 600 eV Hg$^+$ ions are shown in Figs. 2 to 7. Typical cone heights after 4 h of sputtering with 400-eV Hg$^+$ ions at 1-mA/cm^2 ion current density are 10 μ. Thus the cones are much smaller than the ion sheath thickness and one can treat their bombardment as if they were bombarded in a parallel ion beam. The targets acquire in the discharge (3-A, 23-V anode voltage) temperatures in the range of 250° to 350°C. At such temperatures no difficulties arise at the target with formation of a Hg film or amalgamation.

We will summarize what we consider to be established so far without describing the experiments in detail[2]:

1. Even at surprisingly low arrival rates of Mo atoms at the Cu surface (such as 1 Mo atom per 500 sputtered Cu atoms) widely spaced cones begin to appear at the Cu surface.
2. The cone density increases with increasing Mo flux. At arrival rates exceeding 1 Mo atom per 20 sputtered Cu atoms (zone *D*) the cones begin to merge together.
3. The surface of the Mo target where Cu atoms arrive during sputtering shows the usual sputter etching but no sign of cone formation.
4. The phenomenon of cone formation is not confined to Cu–Mo but very similar effects are observed when the Cu is replaced by Ag or Au or when the Mo is replaced by W. Combinations like Cu–Ag or Cu–C show no sign of cone formation.
5. By partial masking of the target one can show that the cones do not protrude above the original surface. This indicates that they are not the result of a growth phenomenon but of sputter protection at selective points.
6. If a Mo film is sputter deposited onto the Cu target before but not during sputtering no sign of cone formation appears.
7. If the seeding with Mo atoms is stopped but sputtering of the Cu is continued the cones break up and eventually disappear.

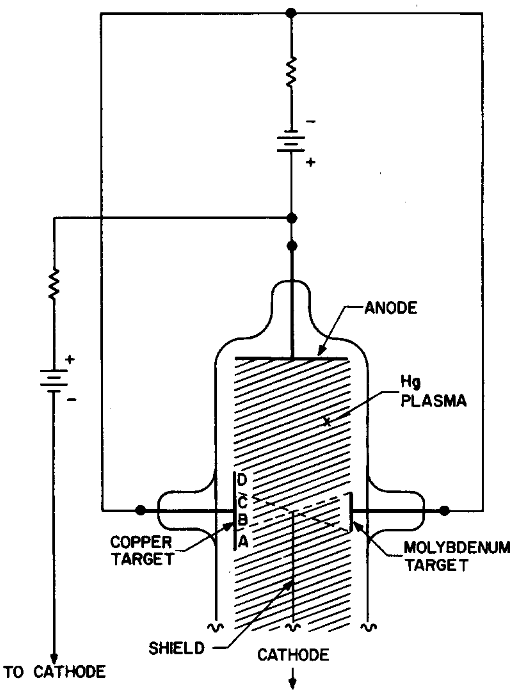

Fig. 1. Electrode arrangement in sputtering section of Hg discharge tube.

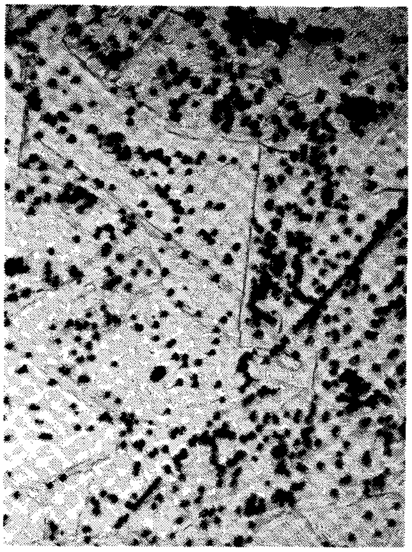

FIG. 2. Optical micrograph taken from zone A (325×) showing cone distribution on variously oriented crystallites and congregation of cones at scratch.

8. Cones appear with different density and with different shape (see difference between center and outer grains of Fig. 2) at differently oriented crystallites. They tend to congregate at scratches and are more abundant at rough surfaces.

9. The question arose if the electric field at the target surface during sputtering in the plasma (dark sheath field) could have something to do with cone formation. By using a fine mesh Mo-screen several millimeters away and in front of the target (keeping both at the same negative sputtering potential and under Mo seeding conditions) one can achieve field free sputtering at the Cu surface. The experiment indicated that cone formation at the Cu surface was not suppressed.

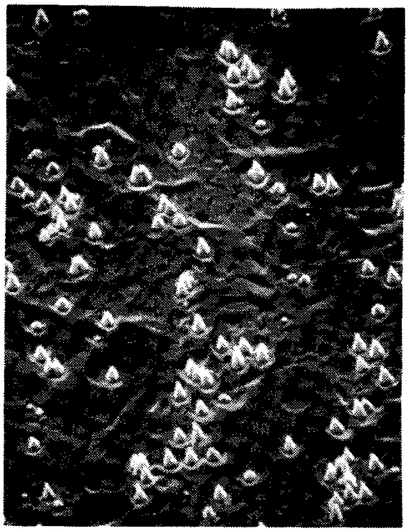

FIG. 4. Electron scanning micrograph taken from zone B (300×).

10. The bombarding ion energy (in the range of 200 to 800 eV) does not seem to be an essential or critical parameter. Although lower ion energy makes it of course necessary to sputter correspondingly longer in order to make the cones clearly visible.

11. As evident from inspecting the target edge where oblique ion incidence prevails one finds that the cones point in the direction of the ion bombardment.

12. Observing and measuring the thickness of sputtered deposits on the tube wall one has to conclude that the angular distribution of material sputtered from a cone-covered surface is quite different from that of a

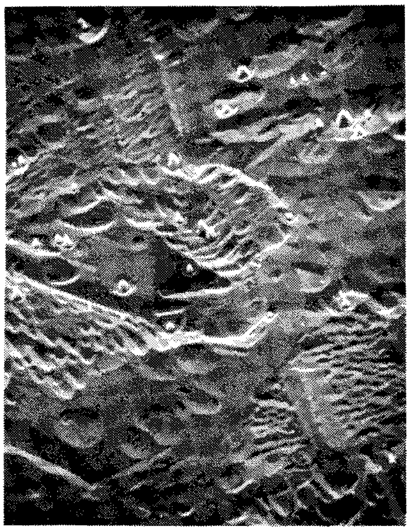

FIG. 3. Electron scanning micrograph taken from zone A (300×).

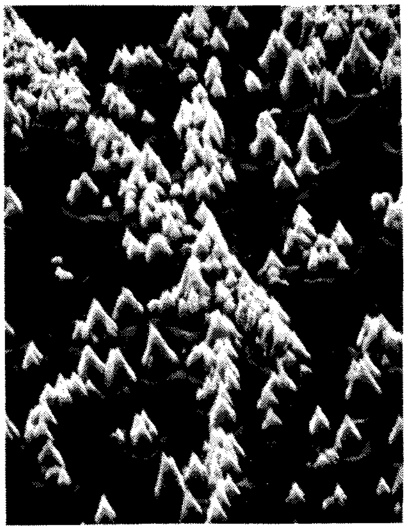

FIG. 5. Electron scanning micrograph taken from zone B (900×).

smooth surface. More material is sputtered obliquely than normal to the target surface.

13. Sparsely distributed cones tend to sit in shallow depressions.

14. Long sputtering runs produce tall hollow cones.

15. To check if surface charging of insulating particles affect cone formation we made some exploratory experiments with rf sputtering. The result showed that cones form just as well as in dc sputtering.

16. Oblique ion incidence promotes cone formation.

The fact that cone formation occurs even under conditions where only 1 Mo atom arrives per 500 sputtered Cu atoms seems to indicate that Mo atoms are difficult to sputter from a Cu surface. One has to conclude that the Mo atoms prefer under ion bombardment or thermal agitation to surface migrate until they find other Mo atoms to attach to. The resulting Mo nuclei which are constantly replenished via surface migration (enhanced by oblique ion bombardment) with new Mo atoms then protect the underlying Cu from being sputtered. In bulk form one knows that under the bombardment conditions in our experiments the Cu is sputtered about 3 times as fast as Mo under normal ion incidence.[3] One may be led to believe that conditions for cone formation arise whenever one seeds a high sputtering yield material with a low-yield material during sputtering. This however is not always true as the combination Cu–C demonstrates. Probably the solubility or the activation energy for surface migration of the low-yield atoms on the high-yield material play additional roles.

With the shield removed we made a number of sputtering yield measurements by determining the weight loss under controlled ion flux and energy. The results were as follows: At 600 eV the yield at the Mo electrode when sputtered alone was 0.9 atoms per ion. The Cu electrode sputtered alone gave a yield of 2.6 atoms/ion. Both results are in good agreement with earlier yield measurements.[3] When both electrodes are sputtered together one has to make a correction for the weight gain from deposition of material from the other electrode. Taking this into account (the gain in our geometry amounted to about 5% of the weight loss) and after a dense cone coverage had been established at the Cu electrode it was found that the yield from the Cu electrode dropped to 0.9 atoms/ion while that of the Mo electrode increased to 1.0 atoms/ion. It is not surprising that a densely cone covered surface has a much lower sputtering yield because the atoms tend to be sputtered back and forth in between the cones but only few of them are able to clear the surface. This was in fact already the subject of a study by Guentherschulze and Tollmien in 1942.[4] Considering that atoms tend to be sputtered in a forward direction[5] it is not surprising either that those atoms which are sputtered from the cone sides and able to escape tend to be ejected much more obliquely than from a flat smooth surface. Whether the Mo yield actually increases when its surface is seeded with Cu needs to be established with further experiments.

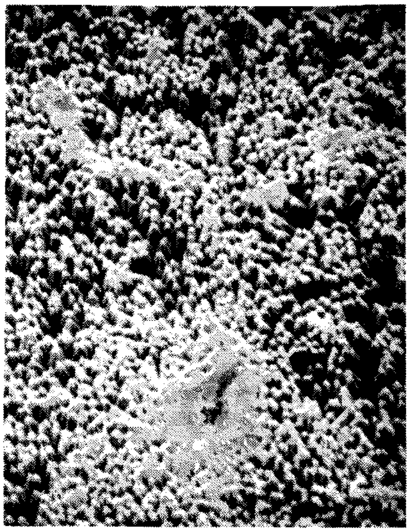

FIG. 6. Electron scanning micrograph taken from zone C (300×).

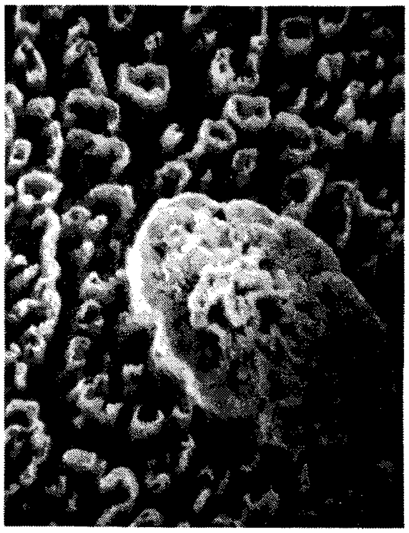

FIG. 7. Electron scanning micrograph taken from zone C after very long ion bombardment (300×).

The cones show characteristic angles between sides of (after correction for the 45° viewing angle) roughly 33 degrees. Small polycrystalline spheres of certain materials such as Mo when bombarded in an ion beam reach an equilibrium cone shape with the cone angle determined by the angle of maximum attack.[6] One might be tempted to link the observed cone angles of 33° to the dependency of the sputtering yield on angle of incidence like in the ion beam sphere experiments. But the situation is widely different between a single sphere in an ion beam and a cone sitting on a flat surface because in the latter case one cannot neglect the modifications which must arise from the sputter deposition and surface migration of atoms from the surrounding surface to the cone sides.

It is of interest to compare the two extreme cases: (a) Cones on a flat surface of materials with a higher sputtering attack under oblique than under normal incidence (like Ta, Fe, Mo) and (b) cones on a flat surface of a material where the attack is highest at normal incidence (like Cu, Ag, Au) ("attack" instead of "yield" was chosen in order to indicate that the reduced current density under oblique ion incidence is taken into account). In case (a) cones cannot persist and should disappear during sputtering while in case (b) the cone covered surface is more stable because the cone sides loose the least amount of material. This general tendency is indeed observed and especially Au targets are known for their tendency to develop stable cone-covered surfaces.

The appearance of cones on glow discharge cathodes of certain materials (Mg, Zn, Cd, Al, Sn, Pb, Sb, Bi) has been observed and described by Guentherschulze and Tollmien.[4] Later Stewart made some impressive photographs of such cones with an early model electron scanning microscope.[7] Stewart and Thompson[8] believe as postulated earlier by Guentherschulze that the cones arise at places where foreign low sputtering yield or insulating particles protect the underlying material from being sputtered. Our seeding experiments show that the cones can also arise from singly distributed "foreign" atoms which then surface migrate together to form the protecting nuclei. It should not matter therefore if the foreign atoms are supplied during sputtering from another source or if they are atomically distributed in the high sputtering yield target material. Indeed, if one sputters an alloy like Cu with 2.5% Be the surface of this target material becomes covered with closely spaced cones just as if the Be were supplied from a separate Be target during sputtering.

The shallow depressions surrounding the more sparsely spaced cones such as noticable in Figs. 4 and 5 are probably the result of increased sputtering by neutralized ions which were reflected downward from the side of the cones. Once in a while a cone loses its protective top, it then becomes round and disappears leaving behind a shallow pit at the place where a cone was originally located. New young cones can of course form at new nucleation sites during sputtering.

Cones finally become hollow as seen in Fig. 7 when they become so large that surface migration is not sufficient to carry the replenishing Mo atoms to the top of the cones and the low sputtering yield protective top disappears.

Heil[9] observed an interesting yield reversal when he used wires of certain different materials which were wound side by side around a core as a target. In Fig. 8 we show such a target (equal diameter of Mo and Cu wire) after long sputtering. The picture shows that the Mo wire is sputtered more rapidly than the Cu wire confirming Heil's observation. Only at the leading edge of the Cu wire where no Mo atoms arrive the higher attack rate of the bare Cu becomes noticable. The wire diameters were small with respect to the ion sheath thickness. This creates a different situation from the previously described experiments insofar as the angle of incidence of the ions varies and only at the leading edges is the ion incidence normal to the surface. This beam-like bombardment situation and the variation of sputter attack with angle of incidence of the ions is responsible for the roof shape which the wires assume. In the sphere experiments[6] we found that more oblique angle of incidence increases the yield in Mo much more than in Cu. Thus the fact that the Mo wire is sputtered more rapidly than the Cu wire is not surprising and this would probably occur even if cone formation was not present.

It will be important to extend the studies to other materials and to learn what influence the target temperature has on cone formation. With Auger spectroscopy we hope that we can show conclusively that Mo atoms are difficult to sputter from a Cu surface and that on a cone-covered Mo-seeded Cu surface the Mo atoms sit mostly at the tops of the cones.

The subject is of some practical interest for a number of reasons: One can produce surfaces with unusual optical or electronic properties (low-electron reflection, highly absorbing surfaces) or surfaces with very high surface roughness. One may find alloys where the formation of cones during sputtering leads to very low-sputtering yield materials. One has to conclude from these experiments that it is often not justified to apply bulk sputtering yield data to the case of alloys. In Auger spectroscopy for instance one uses ion bombardment frequently for removing surface films and measures or estimates their thickness by using bulk yield values. One should be aware of the fact that cases exist where an atom species is more difficult to sputter from

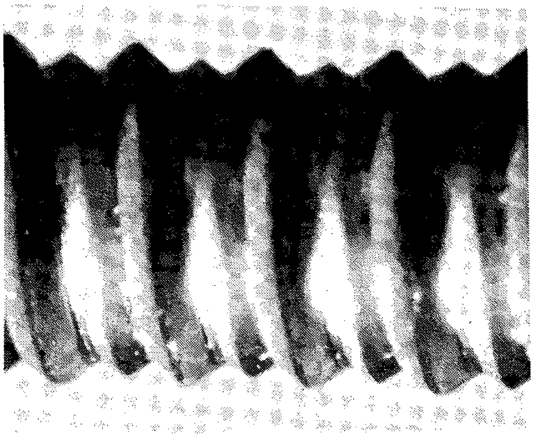

FIG. 8. Optical micrograph of sputtered Cu and Mo spirally wound wire target.

a surface of another species than of its own. If one attempts to sputter simultaneously different target materials for depositing multicomponent films one may encounter cone formation with radically different and changing sputtering yield ratios. Even fairly small amounts of certain impurities in high-sputtering yield materials (such as Cu, Ag, Au, Sn, etc.) can promote cone formation at the target surface. Cones are often the cause for field emission induced sparking at the target. If this is to be avoided one needs very pure target metals. If one sputters high-yield materials one should avoid the use of certain low-yield materials in holders, shields, guard rings, etc. exposed to ion bombardment even if these parts are not in line of sight of the target. The velvet-like dark appearance of the target surface after long sputtering (the darkishness has often been mistaken for carbon deposits) is an easy to recognize indicator of this cone formation phenomenon.

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Low-Energy Electron Beam Studies in Thin Aluminum Foils[*]

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The transmission of normally incident electrons through aluminum, which has been vacuum deposited on a 75-Å aluminum oxide insulator has been measured for electrons of energy between 1 eV and 4 keV. Currents to the top layer (65 to 525 Å) and to the metallic bottom layer underlying the insulator were monitored with operational amplifiers in obtaining the transmission characteristic. Below 50 eV the transmission is apparently controlled by the aluminum oxide insulator. Above this energy the absorption increases rapidly until the entire beam current is absorbed in the top layer. At still higher energies the current to the top layer decreases through zero to a value of −1 (normalized). The energy at which the top current goes to zero was found to increase as the thickness of the top layer was increased. These data were analyzed to yield the electron stopping power which was found to vary from about 3.1 eV/Å at 300 eV to about 4.5 eV/Å at 950 eV when the raw data were corrected for nuclear scattering by a modified version of the Yang scattering theory.

INTRODUCTION

The transmission of electrons through thin metal foils, particularly aluminum foils, has been the subject of many hundreds of papers over the last few decades. Until recently, such studies had been confined to the energy region above a few kilovolts. But, since 1962 many papers have appeared dealing with electron mean-free paths at energies within a few volts of the Fermi level. In these studies, attenuation lengths of the order of 100 Å have been found for metal foils of similar thickness deposited on either insulators or semiconductors.[1–10] By depositing the metallic films on substrates the experimenters were able to go to the minimum foil thickness required for conductivities approaching bulk values across the foil surface. These experiments and the theory for the interactions responsible for electron attenuation at these energies have been reviewed in a recent publication.[11]

When one compares the references noted above with the vast literature for energies above a few kilovolts, one notes a gap in the knowledge of the transmission of electrons in metals in this intervening region. Aside from transmission information which is of some engineering importance, one would hope to determine also electron range, stopping power, and some knowledge of the types of interactions electrons experience with inner shell electrons as they traverse the material. For example, electron range has been measured only to about 1-keV electron energy[12] and preliminary measurements of stopping power in this same energy region have been reported somewhat later.[13] Of particular interest are studies in free electron-like metals where electron interactions are reasonably well understood and where one expects to find evidence of plasmon production. Thus, we were led to choose aluminum, the most studied (as far as electronic properties go) of all metals.