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WHISKERS, CONES AND PYRAMIDS CREATED IN SPUTTERING BY ION BOMBARDMENT

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This status report with minor modifications and additions is intended to become a major publication in Journal of Applied Physics. The authors will be: G. K. Wehner, P. Yurista, S. Bhatia, University of Minnesota and C. Hovland, Physical Electronics Industries, Eden Prairie, Minnesota. Bhatia has earned his MS under this grant. Meyer has finished his experimental work and is presently writing his MS thesis. Yurista has recently started his MS work under this grant. Hovland contributed substantially in his free time with his skill in the operation of Physical Electronics Industries' high resolution SAM. Some contributions were taken from earlier, unpublished MS thesis work by B.Grung and by J. Schwanebeck. In order to make this paper a concise and coherent contribution, we had to eliminate the description of many thoughts and efforts which were conceived in the course of this work, but which turned out to be, in hindsight, either nonproductive or led into deadend alleys. This fact becomes obvious if one compares this report with our rather detailed monthly letter reports which we submitted to our monitor, J. Sovey.

Attached is a copy of the paper "Mass Effects on Angular Distribution of Sputtered Atoms" which resulted largely from our NASA-Lewis support (A. J. Weigand, Monitor) in 1975 and 76. This paper is scheduled for the May 79 issue of Journal of Applied Physics.

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Whiskers, Cones and Pyramids Created in Sputtering by Ion Bombardment.

Abstract.

A thorough study of the role which foreign atoms play in cone formation during sputtering of metals revealed many new experimental facts. Aside from the well-understood cones formed underneath foreign particles, one has to distinguish between two types of "foreign atom" cones: one we call "deposit cones" - the other "seed cones". Deposit cones arise when a lower melting point material [like Cu] is deposited with a certain flux density on a hot, higher melting point target [like Mo] during sputtering. Seed cones arise when a higher melting point seed material [like Mo] is deposited with a certain flux density on a hot, lower melting point target [like Cu] during sputtering. At low bombarding ion energy [< 1 keV] such cones are only produced when the target is at an elevated temperature. Seed cone formation requires a flux density of seed atoms which is above a certain threshold, although this threshold is extremely small. If seed atoms are provided in the form of internal target impurities, one can clearly observe the difference between a sputtered 99.999% Al, which remains cone-free and a 99.99% Al target, which becomes cone-covered after sputtering. The seed flux threshold for cone formation is a function of the target's sputtering rate. This explains why, near threshold, those crystallites in a polycrystalline target material which are oriented such that they have a high sputtering yield remain free of cones while others with low sputtering rate become densely covered with cones. It furthermore explains why cones formed while seeding near the seed flux threshold do congregate in scratches or indentations or in fact at all places where back-and-forth sputtering reduces the sputtering rate. It was found that seeding, even below seed flux threshold, interferes with the usual sputter etching insofar as the sputter rates of differently-oriented crystallites become more uniform and the whole surface becomes covered with ripple-like features.

We tested twenty-six combinations of metals for seed-cone formation and found that in the 17 positive cases the seed metal always had the higher melting point. Seven cases of seed cone formation were found in which the bulk sputtering rate of the seed metal is lower than the bulk sputtering rate of the target metal! Among the nine negative cases were seven in which the seed metal had the lower melting point, one case [Co, M.P: 1493 on Ni, 1452] where the melting points are very close and only one case [W, 3410 on Mo, 2610] which is exceptional. But this latter case will probably follow the melting point rule when one raises the target temperature to a much higher value [as was already demonstrated by O. Heil].

In a separate set of experiments, we measured the sputtering yield variation with composition for combinations which form seed cones. Small amounts of Mo in Cu cause the sputter rate of Cu to substantially decrease, but in the case of Ni-Cu, one finds a linear transition from the pure Cu to the pure Ni sputtering yield. The latter result disproves the idea that seed cones are formed because metal mixtures have an unusually low sputtering yield.

The most rewarding results were obtained with a high resolution Scanning Auger Microprobe. Composition analysis of cones on Cu produced with Mo seeding showed that cone sides and cone tops contain much more Mo than the flat area surrounding a cone. It seems, however, that the Mo enrichment is more the result of a cone sticking out from the surface than being the reason for its creation. This is substantiated by the fact that on a cone which was produced on Cu by Ni seeding, Ni was not detectable at all.

Interesting in situ topography changes are observed in the SAM, when used in the SEM mode, after sputtering by one or two ion beams. It was shown that cones disappear after longer sputtering when no more seeding is provided. Although cones are very rarely found above the target surface, it becomes more and more evident that many details of seed cone formation cannot be explained with a "left-standing" phenomenon only, but a growth process must be involved.

We demonstrated that whisker growth becomes a common occurrence when a low melting point material [like Cu] is sputter deposited on a hot non-sputtered high melting point electrode [like Mo]. We showed that subsequent ion beam bombardment of such whiskers in the SAM converts these into cones pointing approximately in the ion beam direction.

Study of the whisker literature reveals that, in whisker growth, traces of foreign atoms play often a decisive, although not yet well-understood role. Most relevant to the seed- and deposit-cone phenomenon are those whiskers which grow at their base. Characteristic of this specific growth mechanism is the fact that these whiskers grow only when a rigid [higher melting point] substrate or particle is involved.

We are currently pursuing studies with in situ seeding and sputtering in the SAM and of very low ion energy [< 100 eV] seeding and sputtering in a plasma such that the growth predominates over sputtering. Both studies, indeed, seem to indicate that whisker growth plays a dominant factor in both seed- and deposit-cone formation.

Introduction.

Guentherschulze[1] observed in 1941 that glow discharge cathodes of certain metals become covered after extensive sputtering with closely-spaced microscopic cones giving the surface a velvety appearance. He could hardly have foreseen that many aspects of this phenomenon are still, after forty years of intensive research, poorly understood. A pertinent survey "Sputtering-Surface Changes Induced by Ion Bombardment" by Navinsek[2] which appeared in 1976 contains many references on this subject. Navinsek intends to update this with a forthcoming contribution to Volume I of two books "Sputtering by Ion Bombardment", Editor: R. Behrisch under "Topics in Applied Physics", Springer Verlag.

It was established beyond doubt that the maximum in the sputtering yield [atoms per ion] when plotted vs. angle of ion incidence plays an essential role in cone or pyramid formation on sputtered metal targets. If the sputtering yield would be independent of angle of ion incidence, one could not explain the development of well-defined cone angles. In "Analytical Modeling of Sputtering-Induced Surface Morphology" by Carter, Colligan and Nobes[3] the mathematical apsects of this phenomenon are treated in much detail. Certain geometrical construction techniques have evolved [erosion slowness curves, cursors] and with computer iteration programs attempts were made to predict the development of contour changes of topographical surface features such as of a sine wave shaped contour. Carter et al. were aware of the fact that correct analytical solutions to the development of surface features are difficult, if not impossible, due to the presence of other modifying effects such as thermally-induced or ion bombardment enhanced diffusion, modification of slopes by deposition of material sputtered from the vicinity of cones, increased sputtering in cone vicinities by ions reflected from the cone sides, etc. We might add to this another complication which so far seems to have never been mentioned: At ion energies in the keV and higher energy region the single crystal sputtering yield varies not smoothly with angle of ion incidence but displays not one but several yield maxima[4]! The authors leave unanswered the question of long-time stability of such cones and admit that the role which small amounts of foreign metal atoms in a host metal can play in cone formation remains obscure. In fact, in a very recent publication by Whitten, Tanovič and Williams[5], it was claimed that "The dominant parameter contributing to pyramid production is crystallographic rather than impurity-induced", which is contrary to what we[6] and other authors[7] found. For clarification it should be emphasized here that "impurity" is meant to be atomic rather than in the form of microscopic particles. The particle case, where cone formation results from protrusions or from foreign microscopic low sputtering yield or insulating particles is well explainable. SEM observations of the sputter etch phenomena at the edges of resist patterns in ion milling of microelectronic devices have contributed much to the understanding of these particle protection phenomena.

Since 1971 when we discovered the important role of atomic impurities in the cone formation phenomenon[6] it has remained very puzzling why such extemely small amounts of certain foreign atoms can play a decisive role in cone formation. We reported, for instance, that the ratio of Mo "seed" atoms supplied to a hot Cu target surface during sputtering compared to the Cu atoms sputtered from this target can be as small as 1:500 for inducing cone formation. Yurasova's group at Moscow State University found that the few Ti atoms sputtered from the ion beam shaping diaphragms in their ion gun were responsible for cone formation on pure Cu single crystals[7]. Some other important experimental facts are: The phenomenon is particularly well pronounced on high sputtering yield metals [such as Cu, Ag, Au] when seeded with low yield atoms [such as Mo, Ta, Fe]. The cone density is determined by the magnitude of the flux of arriving seed atoms. One can rarely detect cones which protrude above the original surface. Cones appear with different densities and shapes at differently oriented crystallites. They tend to congregate at scratches and disappear after longer sputtering when the seeding is stopped. We and many others had no other choice than to conclude that the seed atom species must be agglomerating into islands which then protect the underlying material from being sputtered as in the particle case.

What concerned us, however, was the fact that one cannot find a believable process which would bring a sufficient number of seed atoms to the cone sides or cone tops for replenishing those that are sputtered away. What concerned Yurasova et al. was the fact that cones come often in closely-spaced clusters: "How can it be that such a narrow slit between the cones is sputtered?".

They came to the conclusion that in combination with surface migration of atoms and sputtering some "growth" process must be involved!

Additional facts were revealed in experiments described in the following sections. These led us more and more towards the belief that Yurasova's statement must be correct and sputter protection alone cannot explain these seed cones. Indeed we could finally prove that whisker growth plays an essential role in this phenomenon.

Experimental.

Experiments were performed under widely-varying sputtering conditions with the following types of equipment:

a. Large area multiple beamlet Ar and Hg ion thrusters with 1 keV ions, space charge neutralized with electrons, ~ 2 ma/cm^2 ion current density, Ar gas pressure in sputtering chamber 10^{-2} to 10^{-3} Pa.

b. Argon RF diode sputtering system ~ 1 Pa Ar pressure, up to 1 keV Ar ions, ~ 3 ma/cm^2 ion current density.

c. Argon DC triode system. $\sim 5 \times 10^{-1}$ Pa Ar pressure, up to 1 keV Ar ions, ~ 2 ma/cm^2 ion current density.

d. Single Ar ion beam with 5 keV ions, $\sim .6$ ma/cm^2, at a Ar background pressure of 5×10^{-3} Pa as provided in the Scanning Auger Microprobe.

e. Hg diffusion-pumped triode system with Hg pool-type cathode creating with a 3 to 5 amp discharge a magnetically-enhanced Hg plasma with up to 20 ma/cm^2 ion current density at $\sim 10^{-1}$ Pa Hg gas pressure. Details of this apparatus have been described in the literature[8].

Surprisingly, [in agreement with results from Yurasova's group who studied cone formation with three widely different arrangements in which they covered the energy range from 100 eV to 40 keV] most aspects of cone formation, except required target temperature, were found to be very similar. Because our studies did not require the creation of cones over large areas and we became concerned about the W atoms sputtered from the neutralizer filament, we switched soon from the thruster approach [a] to the more versatile arrangements [c] and [e]. Arrangement [b] was soon abandoned because interpretation of results becomes more complicated if one deals with ion energies which oscillate between zero and the maximum [1 keV] value and with the required rather high gas pressure which causes backscattering of sputtered atoms.

By far the simplest and most versatile apparatus was our old workhorse, that is, the demountable Hg plasma tube [e]. The Hg pool-type cathode furnishes a contamination-free unlimited supply of electrons and the Hg diffusion pump is, without a trap, directly connected to the Hg discharge tube. This provides high pumping speed and no difficulties with gas cleanup or oil vapor contamination. The use of a Hg plasma for sputtering is made very convenient by the fact that the Hg gas pressure is $\sim$0.13 Pa at a typical water temperature of 17°C, at which the lower part of the tube is kept. This pressure corresponds to a mean-free path of $\sim$3.5 cm for the gas-or sputtered-atoms. When the flat target is large compared to the ion sheath thickness, the ion bombardment occurs under normal incidence. From observations at the target edges one can obtain some information on the effects of oblique ion incidence. With ion current densities of 20 mA/cm^2 at > 300 eV ion energy [> 6 W/cm^2] the target assumes temperatures of > 400°C. At such temperatures there is no chance that Hg atoms would be adsorbed at the target surface. However, measurements at target temperatures of < 200°C [which the target assumes at bombarding ion energies of < 150 volts] become meaningless in a Hg plasma because the dwelling time of Hg atoms at the target surface becomes sufficiently long to interfere with the sputtering process. For such measurements we had to switch to arrangement [c] in which an important requirement is that the target is not in line of sight of the thermionic [W] cathode.

Arrangement [d] when operated with only one of the two ion beams (which are normally used for microsectioning in this apparatus) bridges the gap to higher ion energies and provides well-controlled angle of ion incidence in a UHV [with respect to background gases] environment and allows one to perform not only <u>in situ</u> topography but composition analysis studies with a lateral resolution of ~ 2000 Å.

Results.

1) Internal Seeding and Indications of a Whisker Growth Mechanism in Al.

In most experiments we used very pure target metals and provided controlled seeding during sputtering by sputter depositing foreign seed atoms from another source.

Seed atoms, however, can as well be provided by foreign atoms contained in a metal. Certain alloys [like BeCu with 2% Be], unless the targets are well cooled [see next section], are notorious for their tendency to become cone-covered during sputtering. In fact, we are certain that Guentherschulze's cones were the result of foreign atoms in his not very pure target materials.

A very convincing demonstration of the role of internal foreign atoms was obtained in the following experiment: Three Al targets, one with 99.999% purity, another with 99.99% and a third with 98% were sputtered side by side [in one plane] for five hours with 500 eV ions in an Ar plasma. [One cannot use Al in a Hg plasma because traces of Hg on Al cause it to disintegrate rapidly into grayish blooming Al_2O_3 when it comes in contact with humid air.] The striking result in this experiment was that the 5 N Al shows only the usual sputter etching with grain boundary furrows but no trace of the abundant whisker or cone-like features which developed on the 98% Al surface.

Figure 1 shows an SEM picture of the 4 N Al. Here one finds widely separated protrusions. Some look like genuine whiskers, others are likely to be melted-down whiskers since it is difficult to find a mechanism which, under normal ion incidence, would remove material underneath an overhang. That the melted tops are not spherical in shape is probably the result of subsequent sputtering. In fact, one can assume that after melting, these tops were first single-crystal spheres which nucleated from the single-crystal whisker stems. Subsequent sputtering then shaped them into the observed faceted features. The conical thickenings at the bases of these features are in alignment with their protecting tops. They are probably the

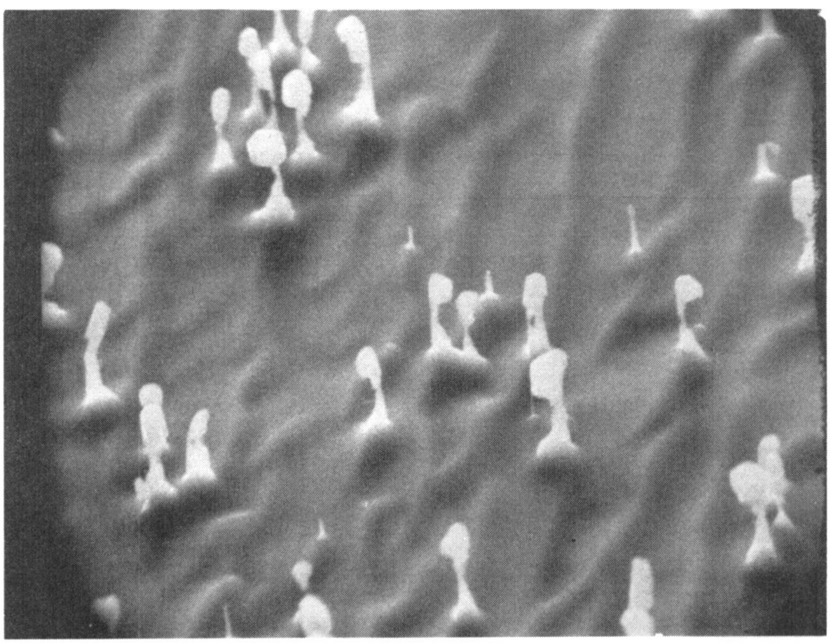

Fig. 1

result of both collection of material sputtered from the vicinity of the whiskers and sputtering of this material before and after the protecting tops had formed. Although the Al target itself did not reach its melting temperature, it is very likely that a whisker, when it exceeds a certain ratio of length/diameter, begins to melt at its top due to the increased ion current current density there, and poor heat conduction of the thin whisker.

2) Target Temperature.

It was found that an elevated target temperature is essential for the formation of seed cones, at least for low bombarding ion energies. This fact was demonstrated in many ways. We sputtered, for instance, a Cu target with Ar ions of 500 eV in arrangement [c] while the target was seeded with Mo atoms which were sputtered from a nearby small Mo electrode. In one case the Cu target was silver soldered to a water-cooled backing plate and assumed a temperature of less than 50°C; in the other experiment the target was thermally insulated from its holder and assumed with 2 ma/cm^2 ion current density [1 W/cm^2], a temperature of about 250°C. In both experiments the sputtering time was ten hours and everything was identical except the target temperature. The cold target remained cleanly etched while the hot target came out velvety black which is typical of closely-spaced cones. The blackness arises in the same manner as in a stack of razor blades when viewed edge-on. The fact that one can avoid cone formation by target cooling is, if course, not a new discovery. In production sputtering for film deposition it has been known for a long time that target cooling is often very essential for achieving a constant sputtering rate. A cone-covered surface has, as already measured by Guentherschulze[1], a substantially reduced sputtering rate.

The temperature which separates the regimes in which cones are formed or not formed seems to be closely related to the melting temperature of the target material. A higher melting point material like stainless steel requires a higher temperature for inducing cone formation. This we demonstrated with a stainless steel target sheet which had the shape of an hourglass through which we passed an ohmic heating current. At the narrow zone we measured a temperaure of 475°C and at both ends temperatures of 325°C. This arrangement was sputtered for ten hours with 500 eV Hg ions at 2 ma/cm^2 current density. The result was that we found densely-spaced well-developed sharply-pointed cones in the hot region of the target only, while in the zones at < 350°C, one could find only the normal sputter etch surface features. In this experiment it was not necessary to provide external seeding - the stainless steel had a sufficient number of foreign atoms to initiate this phenomenon. One can achieve cone formation on stainless steel or Inconel without external heating of the target by raising the bombarding ion energy in a Hg plasma to 1200 eV at 15 ma/cm^2. The 18 W/cm^2 power density brings the target above the critical temperature for cone formation.

3) Cone Growth Above the Original Surface?

In view of the increasing evidence for the involvement of a "growth phenomenon" in cone formation, much effort was devoted to an experiment in which we wanted to check if cones ever extend above the original target surface.

For this purpose a Cu block was mechanically and electro-polished such that it was flat within .5 μm over a distance of 5 cm. The Cu block was masked with two thin flat Cu sheets leaving a 0.5 cm space between them. This assembly was then sputtered while seeding with Mo. After sputtering about 80 μm in thickness with 500 eV Ar ions, (using the masked surface on both sides of the slit as reference level) the target topography was examined under the optical microscope. We found that all cone tops were below the original unsputtered surface and no growth above the original surface seemed to be involved. Unfortunately, this experiment proves little or nothing because cone formation can be an interplay between downsputtering and growth and the 500 eV ion sputtering may have been the dominating factor despite growth in certain specific spots compared to their surrounding area. At this point in our studies we began to recognize that it would be essential to lower the bombarding ion energy in order to reduce the sputtering effects, but somehow maintain the high target temperature which is essential for growth in order to make growth the dominant factor.

It is interesting to relate here back to some never published work which we performed in 1972 and which became B. Grung's Master thesis. At that time the nucleation of sputter-deposited Cu atoms on a hot W wire was studied with the SEM. The W wire was made red hot by electron bombardment in the Hg plasma of arrangement [e].

This was accomplished by using this wire as anode or as partial anode for the 3 amp discharge current. This brings the wire very close to plasma potential. The slowly deposited Cu atoms agglomerate into islands but, as shown in Figure 2, the agglomeration grows often in the form of genuine whiskers. These are mostly straight; we have very seldom seen them kinked but they often change abruptly in diameter. Figure 3, for instance shows a whisker which is thicker at the top than at the lower part. Both parts remained cylindrical but shifted their axis, a phenomenon which is observed rather frequently. We were not able to prove conclusively that these whiskers grow at their base, but it seems unlikely that the whisker with the flag, in Figure 3, grew at the top. We don't know why, but it seems that this kind of whisker growth is confined to sputter deposition. When we deposited with a similar flux evaporated instead of sputtered Cu on the hot W wire, the growth of a whisker became a very rare event.

This whisker growth phenomenon represents, of course, the other extreme from that which is possibly active in seed cone formation - namely, growth without any sputtering.

We observed one other case of "pseudo growth". If one deposits by sputtering onto a hot Mo surface more Cu than is sputtered away [such as with 250 eV Hg ions], one can obtain a coney sputter deposit. Figure 4 shows that these "deposit cones" have more rounded tops and less pronounced trenches in their surroundings.

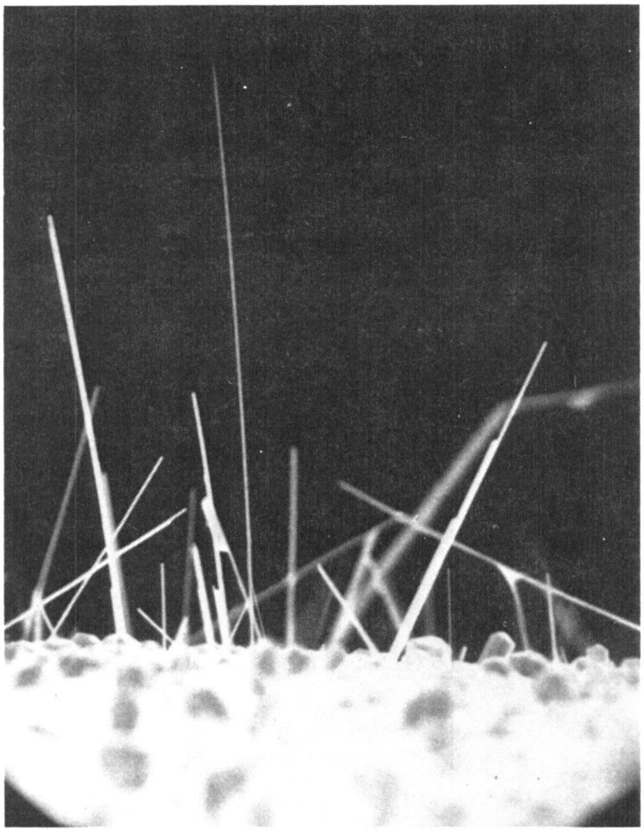

Fig. 2

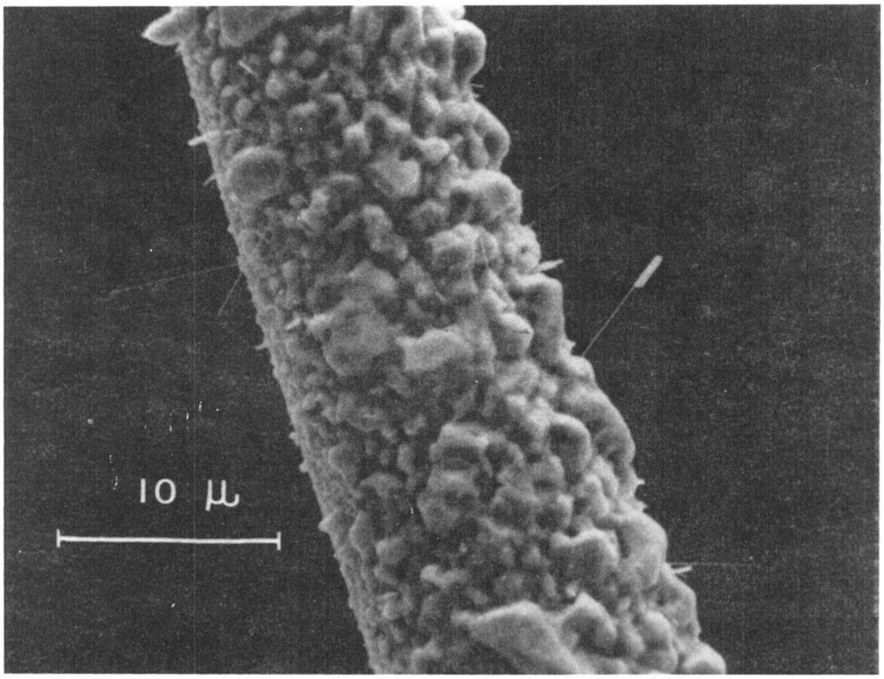

Fig. 3

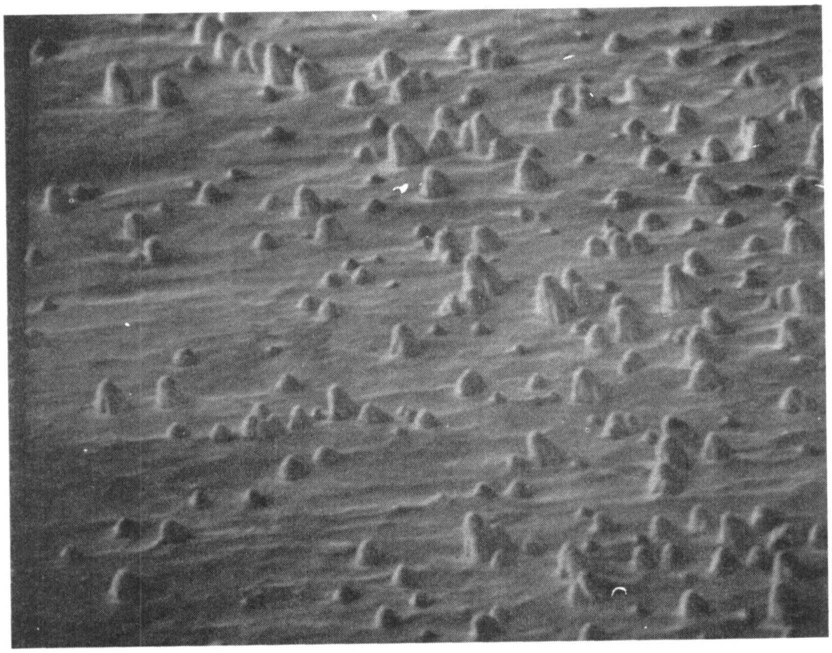

Fig. 4

It became more and more obvious that the most rewarding results for proving the involvement of whisker growth in cone formation can be expected on hot targets bombarded with rather low ion energies where growth begins to dominate over sputtering.

4. Critical Flux Density of Seed Atoms for Cone Formation.

It is surprising not only how small the density of foreign atoms needs to be for producing seed cones but how suddenly cone formation ceases when the seed atom flux drops below a certain threshold value. This situation is very similar to that in heterogeneous nucleation of certain materials, where it becomes impossible to deposit a film, no matter how long one tries, on a hot substrate when the flux density of arriving atoms is kept below a certain value. The critical flux or threshold is most likely a function of many parameters: substrate species, seed atom species, substrate temperature, crystallite orientation, sputtering rate, etc. This subject has so far found very little attention among researchers, although it probably can contribute not only much to the understanding of the cone phenomenon, but has possible practical implications. We found, for instance, that Mo seed atoms sputter-supplied to a hot Cu target during sputtering, even at a Mo flux density which is much lower than the threshold for cone formation, considerably modifies the sputter etching. For reasons which are not yet understood the differences between the sputter rates and in the appearance of differently oriented crystallites become much less pronounced. The whole surface becomes covered with a fine ripple like topography. It becomes, in fact, difficult even after long sputtering under such conditions to recognize, under the microscope, the differently oriented grains. We[6] as well as others[5,7] found experimentally that the cone density can become quite different at differently oriented crystallites. With a seed flux at or near the threshold, one can in fact, observe grains which are densely covered with cones and others which remain completely free of cones. We believe that this is directly related to the variation of the seed threshold flux with sputtering yield. A higher sputtering yield requires a higher seeding threshold for cone formation! We favor this interpretation over the crystallographic one proposed by Whitten et al.[5] for the following reason:

With a diamond scriber we produced indentations and scratches on an electropolished Cu surface. We then sputtered this Cu target while seeding with Mo just below the seed flux density

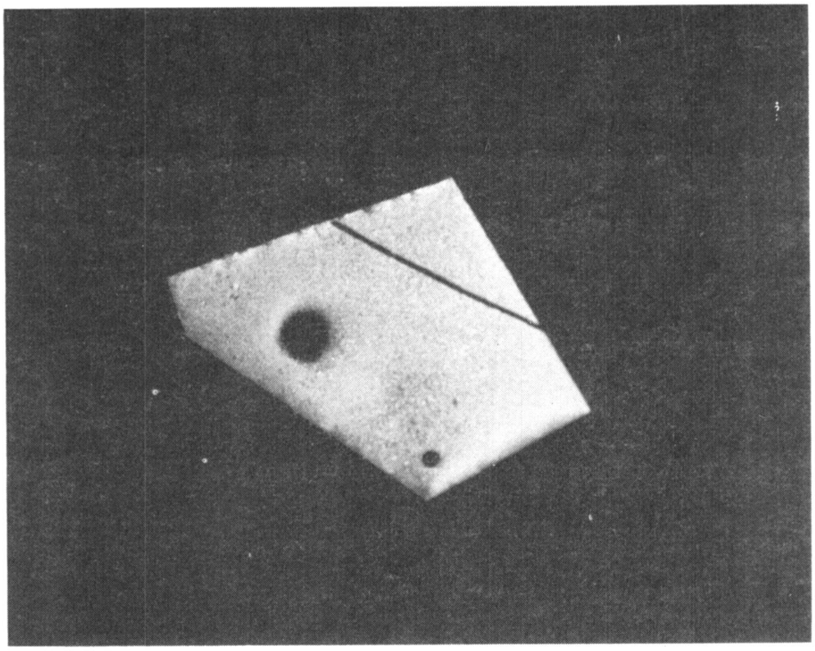

Fig. 5

threshold. As seen in Fig. 5 the result is very striking: scratches and indentations, provided that the target is kept at an elevated temperature, are full of cones and black while the other areas remain metallic in appearance and cone free. With the target cooled, cones appear nowhere. Auger analysis shows only traces of Mo outside an indentation, but considerably more inside. In every scratch or indentation, back and forth sputtering with sputter deposition is involved. The sputtering rate, therefore, becomes smaller and this lowers the seed flux threshold for cone formation.

In the same experiment, if one creates a bump instead of an indentation, one finds that cones are located on the sides of the bump and in a circle surrounding it. If one uses a Cu target which is not a plane sheet but bent such that one part is in line of sight of another, the seed atom flux threshold again becomes lower than on a plane target. It is well known that cones tend to congregate at surface topography features and that electro-polished targets show much less of a tendency to become covered with seed cones. Figure 13, which is described in detail in Section 7, shows an interesting scratch in a Cu target which was mildly seeded with Mo atoms. Three parallel rows of cones developed. In the scratching process the material from inside the scratch was heaved up on both sides. In this way three parallel bands were formed in which back-and-forth sputtering could take place. A very consistent picture, that can hardly be traced back to crystallographic features, emerges from all these observations. At places of lower sputtering rates the seed flux threshold is lower for producing seed cones. What remains to be done is to sputter near the seed flux threshold two targets which are located in one plane with different bombarding ion energies under otherwise identical conditions. One should be able to set the conditions such that the target which is less rapidly sputtered becomes covered with cones.

5. Metal Seed and Target Atom Relationship

By far the simplest arrangement for testing what seed metals or metal atoms produce cones on various pure metals consists of a flat target sheet with a thin seed metal wire wrapped around it.

This target is then sputtered in a plasma or with an ion beam such that atoms from the seed wire are spilled onto the target during sputtering. The seed flux density decreases, of course, with distance from the wire. Visual or microscopic inspection then readily reveals what produces seed cones on what. Very close to the seed wire, in particular when the seed metal has a much higher sputtering rate than the target sheet (such as Cu on Mo), one may find "deposit cones" as shown in Fig. 4. One should, however, clearly distinguish between "deposit cones" which require large deposition flux and seed cones which require very small seed flux. Seed cones are, therefore, found at a much larger distance from the seed wire. Among those who studied seed cones, it was widely believed that the seed atoms must have a lower sputtering rate than the target metal or that they are at least difficult to sputter from the target surface [selective sputtering]. We investigated many combinations of metals and found, to our surprise, that nearly without exception seed cones arise not because the seed metal has a lower sputtering rate, but the seed metal must have a higher melting point! This fact becomes evident from surveying Table I, which lists results at target temperatures of > 350°C obtained with 500 eV Hg ion bombardment for which the bulk sputtering yields are well known. Listed are the melting points (°C) and the sputtering yields $\underline{Y}$ in atoms/ion.

Table I

Seed	MP (°C)	Y(At/ion)	on	MP	Y	Seed Cones
Mo	2610	0.7	Ti	1668	0.4	yes
Mo	2610	0.7	Si	1410	0.4	yes
Mo	2610	0.7	SS	~1400	0.7	yes
Mo	2610	0.7	Ni	1452	0.9	yes
Mo	2610	0.7	Cu	1083	1.7	yes
Mo	2610	0.7	Ag	960	2.5	yes
Mo	2610	0.7	Al	660	0.6	yes
W	3410	0.7	Mo	2610	0.6	no (Heil yes)
Pt	1769	2.0	Pd	1552	1.4	yes
Pt	1769	2.0	Cu	1083	1.7	yes
Fe	1535	0.6	Ni	1452	0.9	yes
Fe	1535	0.6	Cu	1083	1.7	yes
Co	1493	0.7	Ni	1452	0.9	no
Ni	1452	0.9	Cu	1083	1.7	yes
Ni	1452	0.9	Co	1493	0.7	no
Ni	1452	0.9	Pd	1552	1.4	no
Ti	1668	0.4	Ni	1452	0.9	yes
Au	1063	2.5	Ag	960	2.5	yes
Au	1063	2.5	Al	660	0.6	yes
Ag	960	2.5	Au	1063	2.5	no
Cu	1083	1.7	Ni	1452	0.9	no
Cu	1083	1.7	Al	660	0.6	yes
Al	660	0.6	Mo	2610	0.7	no
SS	~1400	0.7	Mo	2610	0.7	no
Pd	1552	1.4	Pt	1769	2.0	no
Si	1410	0.4	Cu	1083	1.7	yes

In those cases in which the bulk seed metal has a higher yield than the target metal, the "yes" is underlined. Some very pronounced cases are Au or Cu seed on Al which produce seed cones but have substantially higher sputtering yield values, while Ni on Pd or Co on Ni in which the seed has the lower yield, produce no seed cones. In general, we found that the greater the difference in melting point, the wider the zone, adjacent to the seed wire, covered with cones. It was somewhat of a surprise that Ni is a good seed material on Cu because we thought for a time that another requirement for seed cone formation would be that the seed atoms are insoluble in the target metal. Table I should be supplemented with Hudson's results[9], who found under 1 keV Xe^+ - ion bombardment no cones for Ta on W, Nb or Mo, but seed cones for Ta on twenty-six other elements. All these elements had melting points below that of Ta. The only exceptions to the rule that a seed metal must have a higher melting point than the target metal exist in combinations of the high melting materials W, Nb, Mo, Ta. This fact is not surprising because neither Hudson nor we [with 2 watts/cm^2] achieved sample temperatures wich are necessary for stimulating surface migration of atoms in these high melting point materials. In a never-published progress report, dated August 1965[10], O. Heil reported that at a much higher target temperature [he used small cylindrical targets in a high density plasma where the bombardment occurred from all sides] he found that W [MP 3410] is a seed material for cone formation on Mo [2610]. We believe that the target temperature [at low bombarding ion energy] should be neither too low nor too high for stimulating the whisker growth which seems to be the essential element in the seed cone formation and probably in the deposit cone phenomenon as well.

Before we discuss this whisker subject in more detail, we should first report on some other pertinent experiments.

6. Sputter Yields of Two Component Metals as Function of Composition.

In the previous section the bulk sputtering yields of the two metals involved in cone formation were listed and found not to play a role in seed cone formation. We are, however, well aware of the fact that the sputtering yields of one species of atoms from neighbors which are not their own kind may be quite different. Very little is known on the overall sputtering yield of alloys or bi-metal mixtures as surveyed by Wehner[11]. The possibility that a small amount of one species [like Mo] in another [like Cu] might drastically lower the overall sputter yield could not be discarded as possibly being responsible for seed formation and cone stability. We started a separate program for measuring the sputter yield of intimate uniform mixtures of Mo with Cu over the whole spectrum from pure Mo to pure Cu. Later such experiments were extended to other mixtures such as Cu-Ni, Al-Au, and Ag-Au. These studies bcame the MS thesis of W. Meyer, and will become the subject of a separate future publication. The interest in this subject extends well beyond the cone phenomenon; for instance, one needs to have knowledge on this in sputter deposition of alloy films or in composition versus depth analysis with in situ sputter microsectioning.

Sputter deposition from two targets in a low gas pressure plasma provided the convenient method for obtaining in one deposition run a film which contains one element on one side, the other element on the other side, and in between all possible mixture ratios spread out laterally. This is accomplished by sputtering the metals simultaneously from two targets which are separated by a shield and depositing the materal onto a flat substrate. With low gas pressure the mean-free path of sputtered atoms is sufficiently large so that sputtered material travels only along the line of sight from the targets to the substrate. The shield is then used to define both atom fluxes such that on one end of the substrate material from only one target is deposited, in the center zone a mixture of material from both targets, and on the other end only material from the second target. A Si wafer mask is placed onto the Si wafer substrate such that a straight step is formed along the whole film composition ratio areas. The substrate is in contact with a water-cooled backing plate in order to minimize volume diffusion in the film and to achieve an intimate mixture of the two species. After deposition of a film which is on the average 5000 Å thick, the step height is measured with a profilometer at regularly marked intervals. The cutup pieces of the substrate are then transferred to the Auger system where one determines the composition versus depth, and in paticular the time it takes to reach the Si interface, i.e., to profile through the previously measured film thickness at the marked intervals. One obtains in this rather straightforward manner the sputtering rate for a 2 keV Ar^+-ion beam of 0.1 ma/cm^2 current density.

The results indicate that as little as 5% Mo can reduce the Cu sputtering rate substantially, but in no composition range did we find that the yield was ever lower than that of pure Mo. In Ni-Cu, which forms a single-phase alloy over the whole composition range, we found that the yield changes steadily with composition ratio between that of the two components. With Ni being a good seed material on Cu for cone formation, but with no sign of a substantial reduction in the sputtering yield of Cu when mixed with small amounts of Ni, we have to discard the idea that this could play a role in seed cone formation.

7. Topography and Composition Studies with the Scanning Auger Microprobe.

In situ SEM topography studies of cones had been first performed by Nelson[12] and later by Broers[13]. Both unfortunately never bothered to published their interesting studies. In recent years commercial instruments became available in which high lateral resolution surface composition analysis is combined with SEM capabilities. The Scanning Auger Microprobe [SAM], in particular, has been developed to a high degree of sophistication and now approaches lateral resolution capabilities of < 1000 Å. We were fortunate to be able to acquire one of the earlier SAM's and it soon became obvious that these instruments were ideally suited for answering many questions which the seed cone phenomenon poses. Obviously one of the most pressing questions was if one could detect substantial differences of seed atom concentrations between cone tips, cone sides and their environment. We put much effort into this task, but with little success due to several shortcomings of our SAM, such as, that the single ion beam impinges on the sample from a different direction than the analyzing electron beam [which causes shadowing artifacts] and in particular the limited lateral resolution [3 μm] of our early version SAM. Fortunately we had access to Physical Electronics Industries' much more advanced SAM, which has not only 10 X higher lateral resolution, but is equipped with many microprocessor and computer-controlled automation and data processing features. Results described in the following were all obtained with the PHI Model 590A SAM System.

We selected a target which was prepared as described in Section 5. The Mo seed gradient had produced a cone density

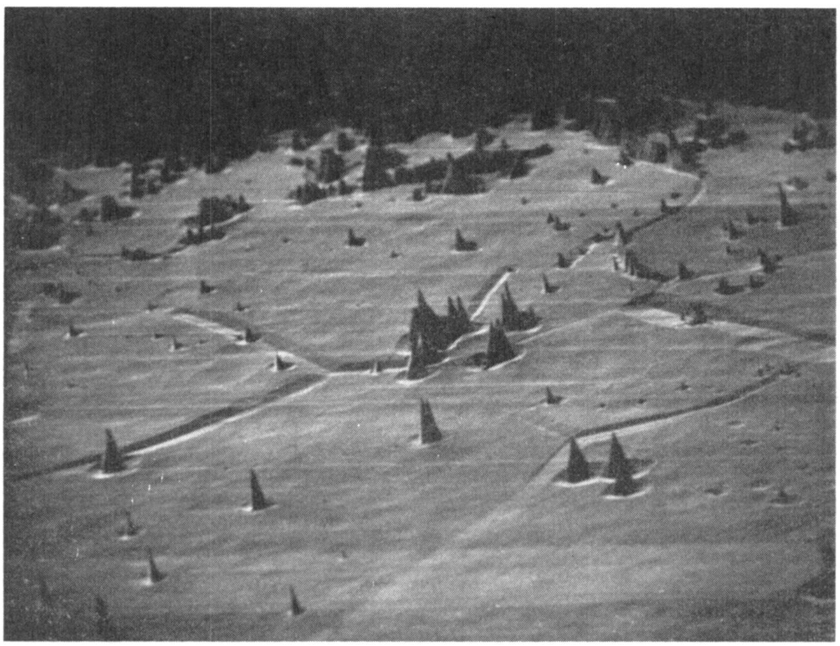

Fig. 6

gradient on the Cu target as shown in Fig. 6 [150 X]. Figure 7 shows a picture of the dense whisker-like cone forest close to the Mo seed wire. The centrally located double or triple cone in Fig. 8 [1000 X] was selected for further detailed studies. Switching to point Auger composition analysis with signal averaging, we measured the Mo surface concentration at the cone tops, cone sides, the surrounding trench, and the flat area away from the cone. Without any pre-sputtering in the SAM, the following percentages of Mo in Cu were found: Cone trench: 3%; cone side: 7%; cone top: 16%; top of small cone at lower left: 13.5%; flat area < 1%. After some very mild sputtering [approximately 10 Å of Cu removed] the Mo had completely disappeared in the flat area; in the trench it had decreased to less than 1%, and at the cone side it had dropped to 4.5%. After about 100 Å of Cu removal, the cone side contains still ~ 2% Mo.

These results confirmed one fact, which we had found much earlier[14], namely that Mo is more difficult to sputter from Cu [or even more so from Al than from W or Mo]. In Meyer's studies, as described in the previous section, it was observed that during profiling of a Cu film, which contained a small amount of Mo, the Mo became much enriched with increasing profiling depth. Beyond doubt, in Mo-Cu mixtures, the Cu is sputtered preferentially. It is, therefore, not surprising that the Mo became, in particular, much enriched in those areas where back-and-forth sputtering takes place, i.e., at locations which are elevated above the adjacent surface. Higher up on such an elevated feature, more Mo is found because it is collected, as resputtered material, from a larger area.

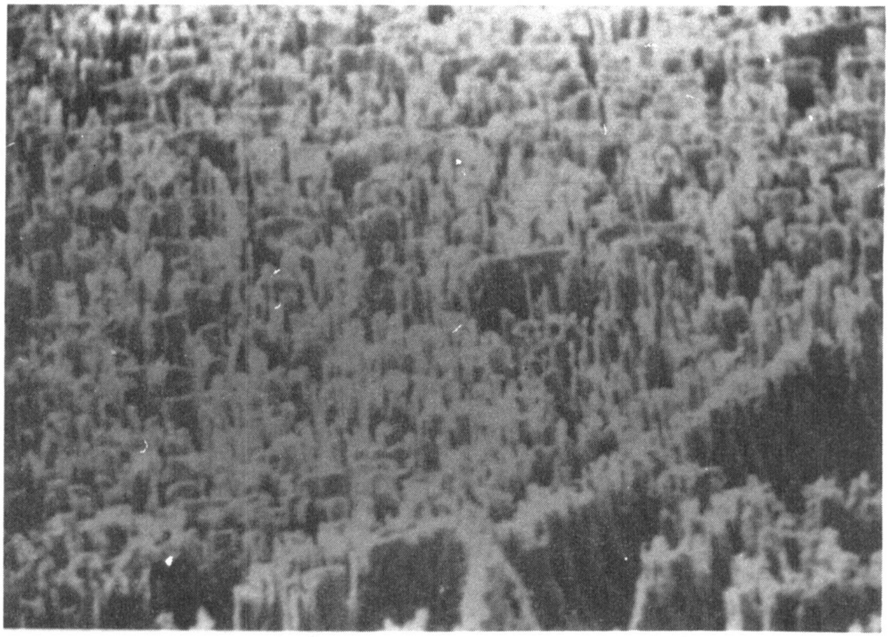

Fig. 7

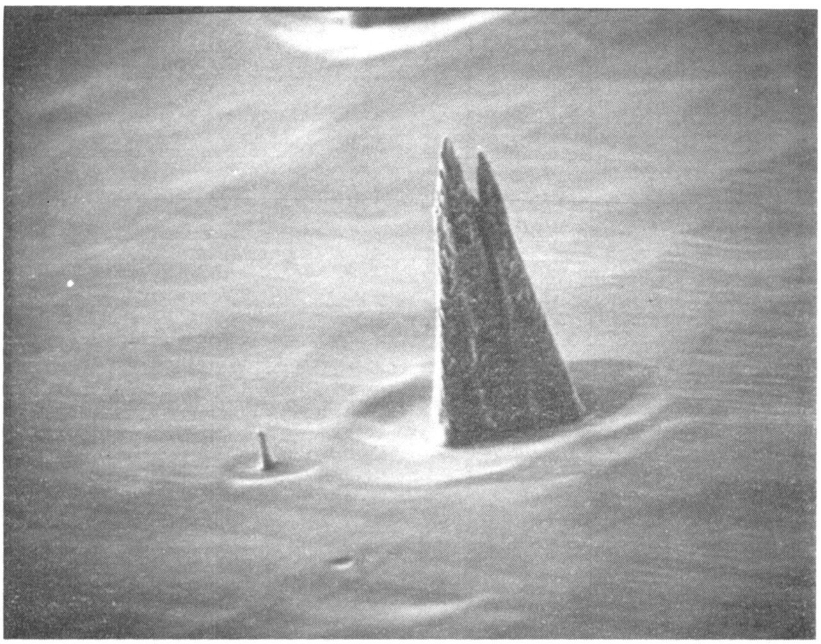

Fig. 8

The interpretation of composition results on the surface of a steep feature like the cone sides after sputtering in the SAM can be misleading because these can become collectors of material sputtered by the ion beam from areas in the vicinity.

It seems as if the Mo enrichment is more the result of the cone sticking out from the surface than being the reason for its creation, although after it is formed, the molybdenum enrichment must contribute to its persistence and stability.

Figure 9 shows the topographical changes which are produced after 12 minutes of sputtering in the SAM with two ion beams which impinge from different directions. The shadows in both ion beams leave their clear traces. Figure 10 depicts

Fig. 9

the same area with the same magnification as in Fig. 6 obtained after an additional two-hour sputtering in the SAM with both ion beams. The landscape [with no Mo seeding - see Section 4!] became much more detailed and the differences in sputtering yield of differently-oriented grains, more pronounced. Of particular interest is the fact that new previously unobserved [sub?]-grain boundaries appeared now very sharply. Figure 11

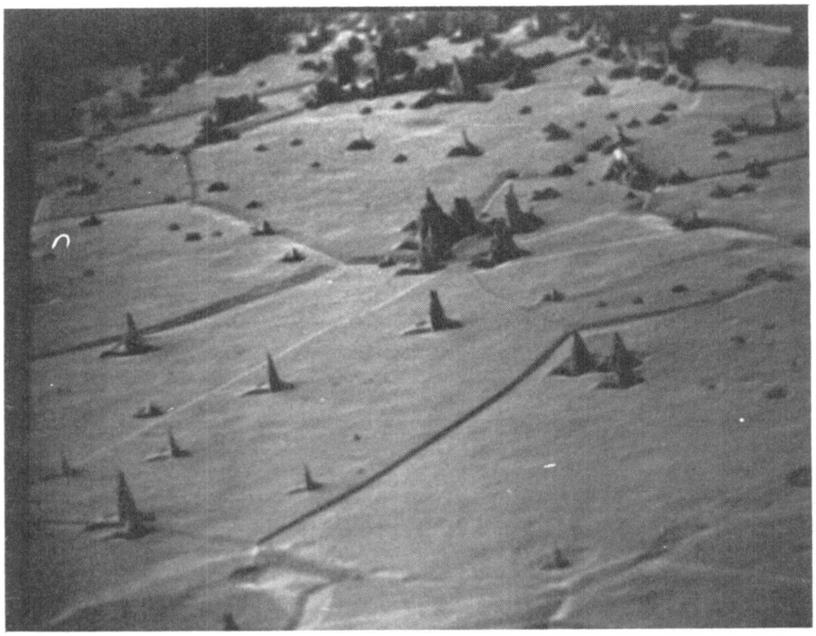

Fig. 10

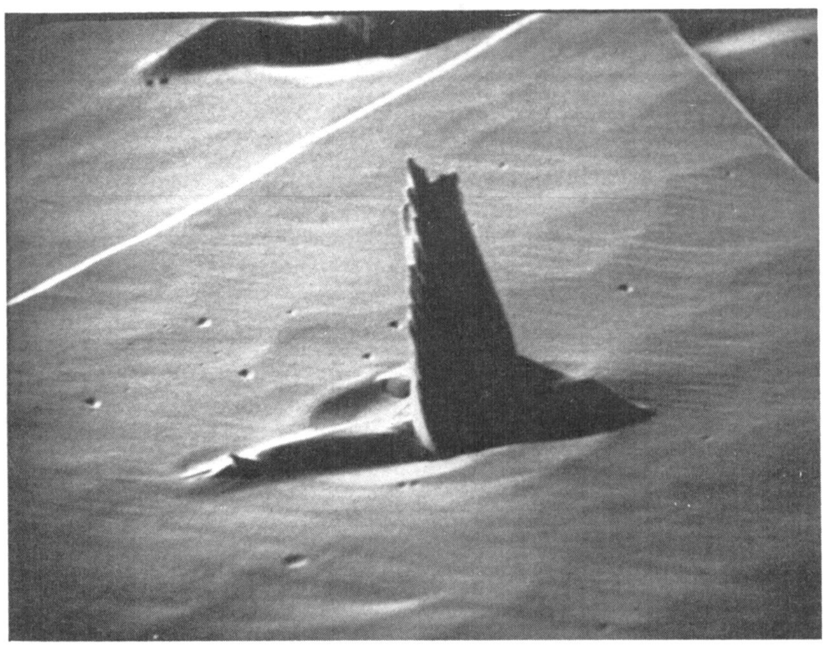

Fig. 11

is the counterpart of Fig. 7. It shows not only the effects of the heavy sputtering, but an interesting feature at the little cone. It was a fortunate inicident that this little cone was shadowed from one of the ion beams by the big cone. This caused the little cone to become reshaped in such a manner that it now points towards the single ion beam to which it was exposed. Yurasova's group was first to point out that oblique cones do not point exactly in the ion beam direction because sputter deposition of material from the cone vicinity is not symmetrical and this modifies the cone angles. Of interest the trench surrounding this little cone. It is obviously caused by enhanced sputtering, resulting from ions or neutralized ions which were reflected very obliquely from the cone sides.

Finally, a 12-hour sputtering run was performed in the SAM. Figure 12 [150 X], which should be compared to Fig. 6, shows man

Fig. 12

details which were never revealed by sputtering during Mo seeding. The fact that even very little Mo seeding equalizes the sputtering rates of differently-oriented crystallites could have practical implications such as in sputter polishing or in composition analysis of interfaces between layers of different materials where the "overburden", if it consists of differently-oriented crystallites, causes artifact broadening at the interface.

Next, the sample as shown in Fig. 12 was transferred back to the Hg stand for further Mo seeding during sputtering and then inspected again in the SAM. The area of our previous studies, indicated with an arrow in Fig. 13 [25 X], was found again and shows a number of interesting features: a. Many details in

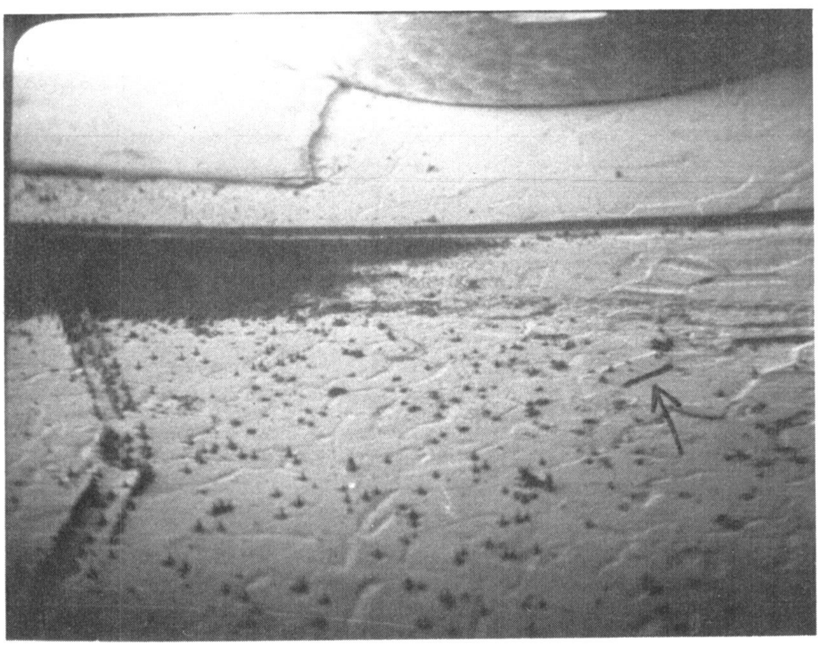

Fig. 13

surface topography, which were brought out under the "no Mo seeding with two ion beams in the SAM" became washed out again.
b. Part of the dense forest which had developed under the high flux seeding close to the Mo wire became denuded and
c. Along a scratch three parallel rows of cones developed as described already in Section 4.

The main area of study is again depicted with 150 X in Fig. 14. It shows rounding of the previously sharply delineated grain boundaries, the formation of trenches along and around elevated features, the appearance of new cones, in particular, at the bottom of slopes or in shallow depressions, the lateral movement of steep slopes toward the elevated side [the elevated grain became much more narrow] and the breaking up of old cones into multiple cones clusters as shown more clearly in the 500 X photograph of Fig. 15. To explain the latter phenomenon without a growth process would indeed be a challenge!

Fig. 14

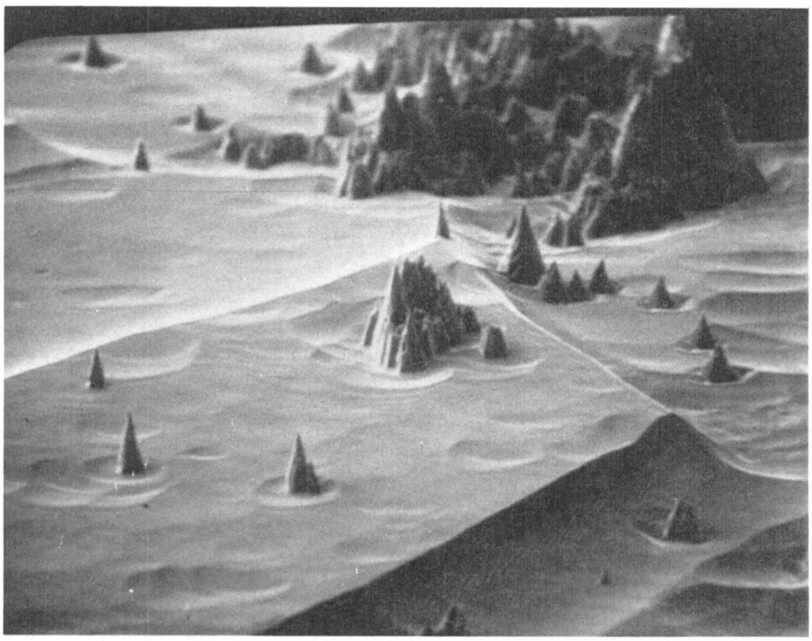

Fig. 15

We repeated composition analysis at various locations and found again that Mo is enriched at cone sides or tops.

We wanted to demonstrate that the cones without Mo seeding eventually disappear and therefore transferred the target once more back to the Hg stand for a heavy final sputtering without Mo seeding. Figure 16 shows the area of our studies.

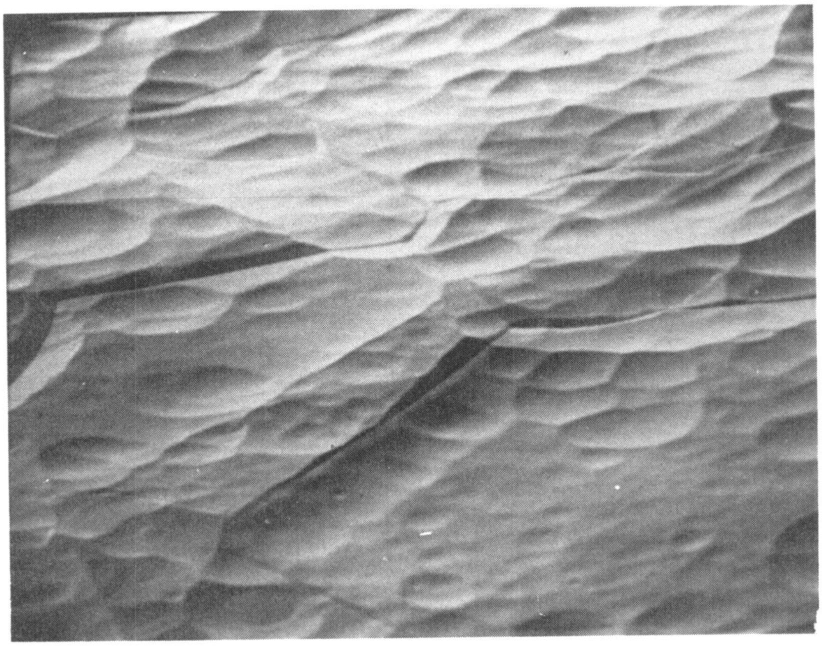

Fig. 16

Cones have indeed completely disappeared. One can still correlate the shallow scopped-out depressions with the locations in which cones used to be located. Somewhat disappointing was the fact that we did not see more details between differently-oriented crystallites. But this may have been the result of the high temperature which the target assumed in our plasma because it became very thin and edge parts of the target were already completely sputtered away.

Ni, contrary to Mo, is soluble in Cu and small amounts of Ni in Cu do not reduce the sputtering yield of Cu substantially but Ni nevertheless is good seeding material on Cu. It, became obvious that we should repeat the SAM composition analysis on cones produced by Ni seeding.

With Ni seeding we found more pronounced differences in cone density between differently-oriented grains [in agreement with what was stated above, grains with higher sputter rate have lower cone density!] and found that the cones are usually not round but exhibit crystallographic contours [pyramids] which are related to the crystallite orientation on which they grew. We intended to compare, as in the Mo-Cu case, the amount of seed atoms found on cone sides, cone tops and cone-free areas. Although the Ni was clearly responsible for the formation of these cones, it was nowhere detectable! It becomes more and more evident that the previously speculated reasons for seed cone formation are not in agreement with this experimental result.

8. Is Whisker Growth Involved in Cone Formation?

We repeated first an experiment which resembles that which led to Fig. 3 [described in Section 3]. A Cu target [at -500 V] is located opposite an equal size Mo target [at -400 V] and both, facing each other at a 4 cm distance, are exposed to 10 ma/cm^2 Hg ion bombardment under which both became dull red. Part of the Mo target was shielded from ion bombardment by a slightly separated thin Mo mask such that the Mo underneath this mask could receive a Cu-Mo mixture deposited from the opposite Cu target. Figure 17

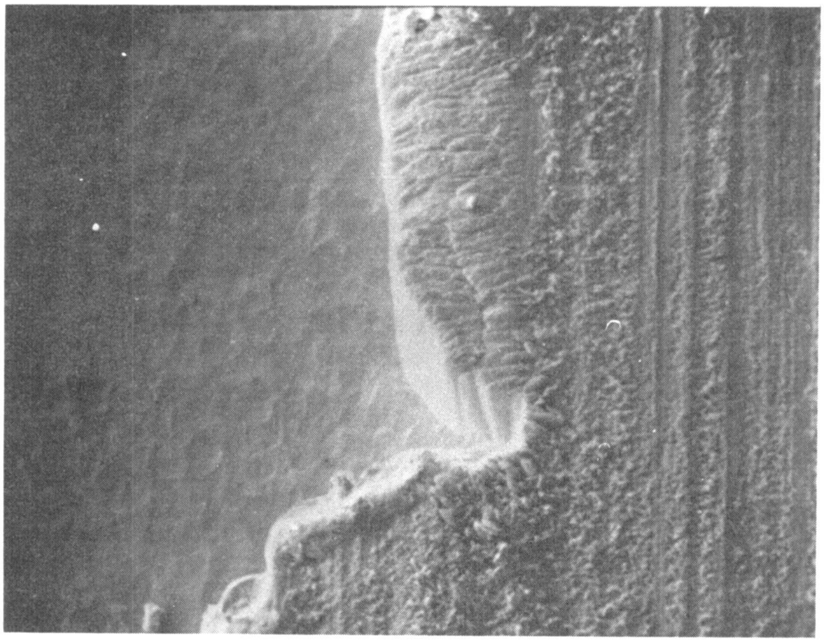

Fig. 17

[1000 X] shows the sharp step between the sputtered [left side] and shielded [right side] Mo target. The unsputtered part close to the dropoff where the Cu-Mo had been deposited on the hot Mo is shown in Fig. 18 under 10,000 X magnification taken in the SAM. It shows profuse whisker growth. These whiskers have most likely grown at the Mo base and consist probably of Cu. This still needs to be proven because SAM analysis of such

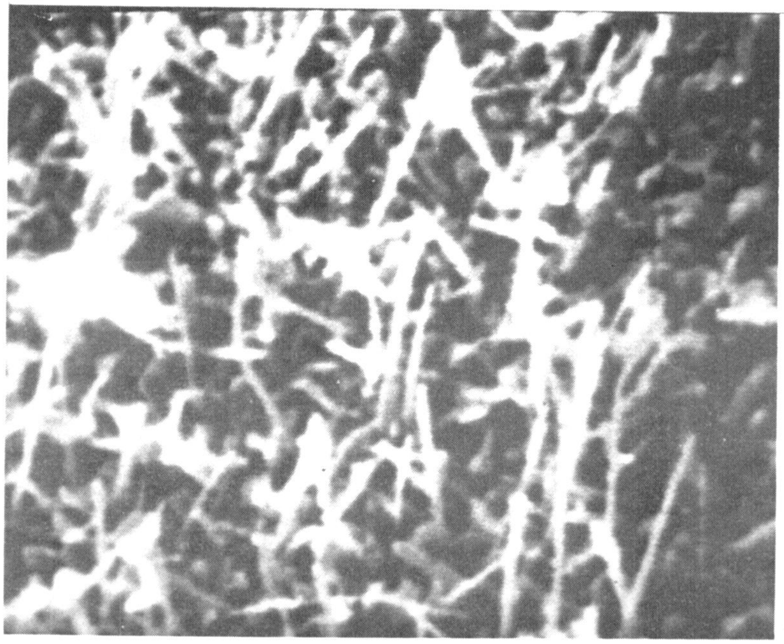

Fig. 18

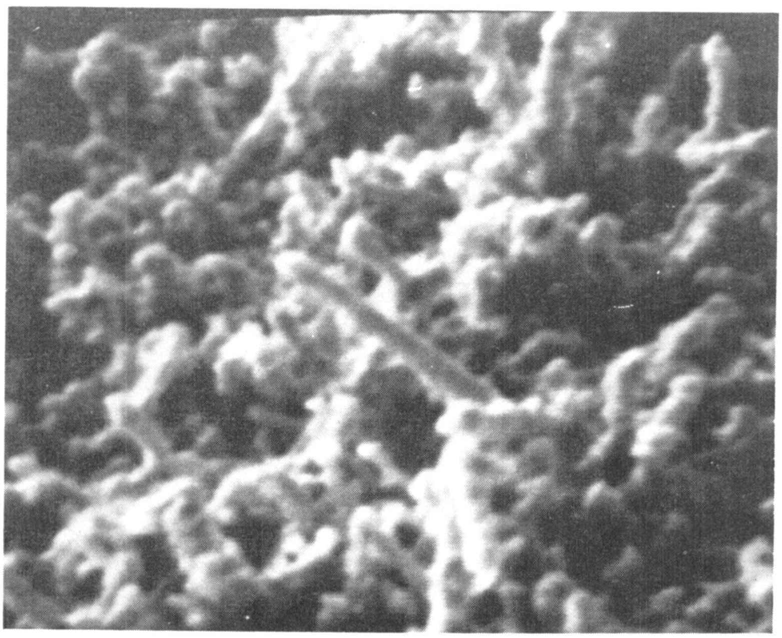

Fig. 19

elevated features leads, as pointed out before, to an artifact arising from the sputter deposition of Mo from the Mo base. For conclusive analysis of these whiskers, one has to shave those off and put them on a substrate of another material which was not involved in their growth such as Al. The whisker-covered area shown in Fig. 19 was now exposed to a short five-minute ion bombarment by one of the ion beams [5 keV] in the SAM. Figure 20 [10,000 X] shows very interesting details of

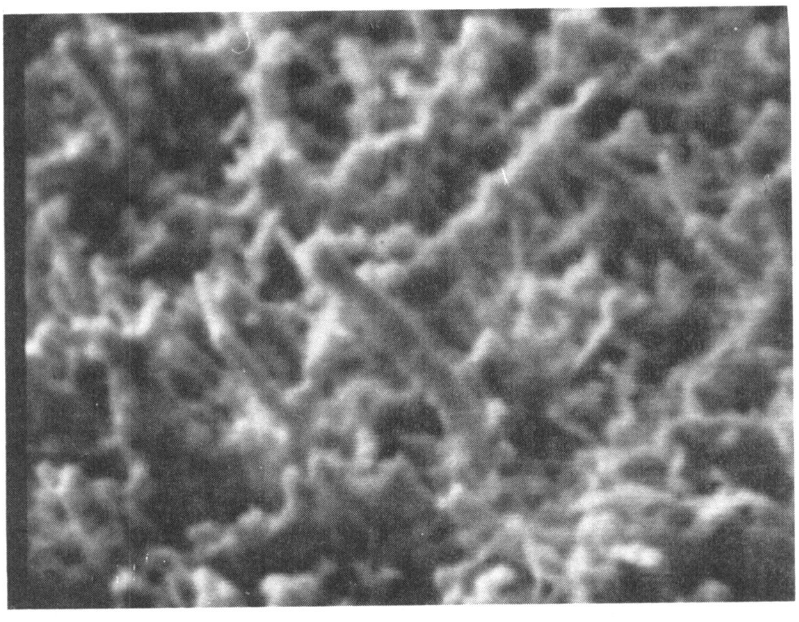

Fig. 20

the subtle changes which this short bombardment produced. The whiskers started to align themselves in the direction of the ion beam [which came from the upper left] and the more exposed whiskers have increased in thickness and many have become slightly more pointed.

Although the ion beam electrode, which determines the final acceleration of the ions, is at the same potential as the target, one cannot neglect the field between the target and the ion space charge, which creates a pulling electric field on the whiskers.

After sputtering an additional 75 minutes the conversion of whiskers to cones pointing in ion beam direction has become complete as shown in Fig. 21 [5000 X]. Needless to point out,

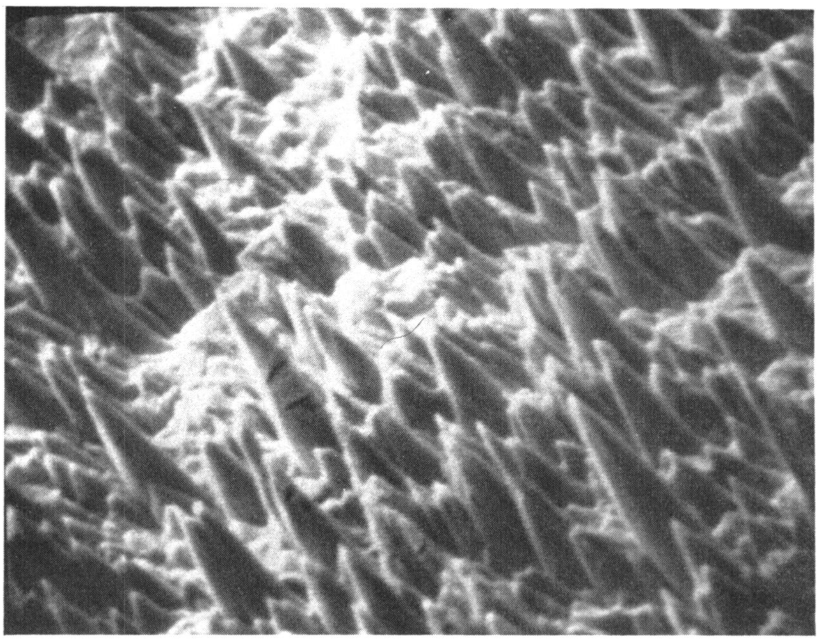

Fig. 21

neither the heavily sputtered area to the left in Fig. 16 nor the area deeper underneath the mask where no whiskers were grown, show any sign of cones.

The possibility of whisker growth being involved in seed- and deposit-cone formation begins to look more and more intriguing. We have often observed cylindrical needle-like protrusions on top of cones. Whiskers can grow rather rapidly out of a surface and will subsequently, under sputtering, become collectors of material sputtered from the surrounding area. Cones could indeed be the result of an interplay between whisker growth, material collection, and ion bombardment etching.

Study of whisker literature[15] reveals that in many types of whisker growth, traces of foreign atoms play a decisive, although not yet well understood role. Most relevant to the sputter seed and deposit cones case are those whiskers [mostly low melting point metals like Sn, Cd, Sn, Bi etc.] which grow at their base. Characteristic of this specific growth mechanism is the fact that these whiskers grow only when a rigid [higher melting point] substrate or particle is involved. Bi whiskers, for instance[16], grow at elevated temperature only in the presence of Mn. Spontaneous Sn whisker growth can readily be observed even at room temperature when metal sheets [from tin cans] are squeezed in a vise. Squeezing pure tin never leads to whisker growth - the rigid steel base for the Sn coating obviously plays an essential role. It is generally accepted that relief of compressive stress, screw-type dislocations and atom movement such as provided by elevated temperature are involved in this type of whisker growth.

Whisker growth is, we are convinced now, not only involved in deposit cones as we demonstrated here, but in seed cones as well. The only difference seems to be that in deposit cones the whiskers grow on the higher melting point base material; in seed cones the whiskers grow on higher melting seed material islands.

We are currently in the midst of two exciting studies:

a. In situ seeding and sputtering in the SAM with cold and heated targets and

b. seeding of Cu with Mo in the Hg plasma, but sputtering the separately heated Cu target at much lower (< 100 eV) ion energy such that growth predominates over sputtering.

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Final report. Project manager, James S. Sovey, Space Propulsion and Power Division, NASA Lewis Research Center, Cleveland, Ohio 44135.

16. Abstract

A thorough study of the role which foreign atoms play in cone formation during sputtering of metals revealed many new experimental facts. Aside from the well-understood cones formed underneath foreign particles, one has to distinguish between two types of "foreign atom" cones: one we call "deposit cones" - the other "seed cones." Deposit cones arise when a lower melting point material [like Cu] is deposited with a certain flux density on a hot, higher melting point target [like Mo] during sputtering. Seed cones arise when a higher melting point seed material [like Mo] is deposited with a certain flux density on a hot, lower melting point target [like Cu] during sputtering. At low bombarding ion energy [<1 keV] such cones are only produced when the target is at an elevated temperature. Seed cone formation requires a flux density of seed atoms which is above a certain threshold, although this threshold is extremely small. Experimental results of this investigation deal with surface migration of atoms selective ion etching as well as microscopic growth phenomena.

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