Surface topography of eroded Cu and Si cathodes in a PIG ion source

A K SEN and D GHOSE

Saha Institute of Nuclear Physics, Sector 1, Block AF, Bidhan Nagar, Calcutta 700 064, India

MS received 1 August 1992

Abstract. The surface topography development on a Cu sheet and a Si(111) wafer was studied after being sputtered in a Penning ionization gauge (PIG) ion source using Ar gas. In the case of Cu, a high density of conical structure was developed on the surface. The most striking feature was that the individual cones, relatively large in size, were often coated with impurity layers. Some cones were decorated with concentric ring-like patterns on their surfaces. The overlying coating was thought to be responsible for the initial growth of the cones and subsequent evolution of secondary protuberances on the surfaces of the cones. In the case of Si, though a few impurity-induced conical protrusions were formed, the dominant morphology was in the form of etch pits. In addition to usual single cones, Si surface developed cones of dimeric structure and cluster of cones.

Keywords. PIG ion source; Ar gas; Cu; Si; sputtering; cones; etch pits.

1. Introduction

When a solid surface is bombarded with energetic ions, surface atoms that receive energy in excess of their binding energy are sputtered from the sample. As the dose of the bombarding ion is increased, the solid surface is eroded successively and some characteristic etch patterns, such as conical protrusions, grooves and pits, develop on the surface of the sputtered area. Textured surfaces formed by ion-beam sputtering have many characteristic properties that make them suitable for a large and diversified number of applications. Auciello (1981) listed the following fields in which texturing has possible applications: (i) microelectronics, (ii) surface acoustical and optical technologies, (iii) solar energy conversion technology, (iv) ion-beam surface analysis, (v) thermonuclear fusion, (vi) field ion emission and electron microscopy, (vii) surface-enhanced Raman scattering spectroscopy and (viii) biomedicine (implantology). Many researchers (Wehner and Hajicek 1971; Berg and Kominiak 1976; Kelly and Auciello 1980; Wehner 1985) have prepared textured surfaces covered with dense arrays of cones in low-gas-pressure plasmas created with RF, or in DC diode or DC triode discharges. The present work investigates the surface topography development on Cu and Si in Penning ionization gauge (PIG) discharge not only to substantiate earlier studies but to obtain new results.

2. Experimental

The ion etching of the samples was carried out in a PIG ion source similar to that developed by Baumann and Bethge (1974). It was a cold cathode end extraction version, the characteristics of which were studied earlier in conjunction with a $\sqrt{2\pi}$ magnetic analyser (Sen and Ghose 1991). The Mo anode cylinder had a length of 20 mm and an internal diam. of 6.6 mm. The two Ta cathode discs were separated

by a distance of 27 mm. Operating data of the ion source were: discharge voltage, V_d , 1–3 kV; discharge current, I_d , 2–10 mA; magnetic field, H , 0.5–0.8 kG; pressure in the source, p , 10^{-3} – 10^{-2} mbar. Since the ions were accelerated in cathode fall, the energy of bombarding ions was $\approx eV_d$.

For the present experiment, one of the Ta cathode discs was replaced by either a 0.5 mm thick electrolytic Cu (purity 99.9%) sheet or a *n*-type Si(111) wafer of resistivity 1000 Ω -cm. Pure argon gas was fed into the source via a calibrated Edwards needle valve. Before ignition, the discharge chamber was cleaned with Ar gas for 30 min. The cathode samples were then exposed to sputtering for 15 min to 3 h. The surface topography of the irradiated samples was examined under different scanning electron microscopes (SEM) such as Philips PSEM 500, JEOL (model no. JSM-840) and CAMSCAN MK-II (UK).

3. Results and discussion

Figure 1 shows the general view of a typical etched sample. The surface developed a number of concentric craters and the steep sides were cut into a regular staircase of terraces. The innermost crater had a size of 3 mm diam, which coincided with the size of the extraction hole of the cathode. The results show that the density of plasma was non-uniform near the boundary and more intense over the region where the ions were extracted.

3.1 Topography of the eroded Cu samples

All the etched Cu samples showed well-developed textures on the surface of the crater. Figure 2 illustrates a typical textured surface following 30 min of etching. The topo-

Figure 1. Electron micrograph of a Cu sample after erosion in PIG discharge for 1 h. White markers = 100 μ m.

Figure 2. Electron micrographs showing high density of cones on an eroded Cu surface; (a) tilt 33.5° and (b) tilt 0°. White markers = 1 μm .

graphy consisted of conical protrusions, the number density of which was so high that the etched region appeared deep red in colour to the naked eye. The mean distance between the cones was about 1 μm , while the mean height was about 5 μm . Figure 3 presents another spot of the etched area, where the big cones situated at the centre of the micrograph appear to have deposit layers at the upper portion. This type of coating was also seen on other cones as shown in figure 4 where some cones had top coverings with a faceted structure. The most interesting observation was that small protuberances developed from the surfaces of the cones. Figure 3 also reveals the formation of bent cones which is clearer from the top view of the structures (figure 5). Where the cone density was low, the additional features developed were the familiar troughs around the cone bases and the facets on the cone sides.

The formation of impurity-based cones is well documented in the literature (e.g. Ghose and Karmohapatro 1990). The presence of impurities is mainly of importance for the first phase of development of cones. During further ion bombardment the

Figure 3. Electron micrograph showing some typical big cones (at the centre) covered with the deposit layer. A few cones are found to be bent near the top (see the lower portion of the micrograph).

Figure 4. Electron micrograph showing big cones with the generation of tiny cones on their surfaces. The arrow marked cones have faceted impurity covers.

Figure 5. Electron micrograph showing the top view of cones having bent apices.

induced microstructures change their shape in a characteristic way, which mainly depends on the variation of sputtering yield with the angle of ion incidence and secondary effects such as ion-reflection, redeposition and surface diffusion. In the present experiment, the possible sources of impurities are the sputtered Ta materials from the anticathode and condensed cracking products from low vapour pressure hydrocarbon molecules. Energy dispersive X-ray (EDX) analysis which is sensitive only to high $Z(> 11)$ impurities, shows the presence of Ta at the level of 1 at %.

Alexander *et al* (1981) detected carbon impurities at the top of lead cones. Whitton *et al* (1984), while studying a number of f.c.c. metals, found that impurity-induced cones were larger in size than defect-induced cones. In the present experiment, relatively big cones have impurity coatings on their surfaces. This type of cone was first reported by Rossnagel and Robinson (1981, 1982) and Robinson and Rossnagel (1982). They noticed that cone size tends to increase as long as the coating is in place, but cones begin to shrink if there is a failure in the coating; the coating serves to protect the cones from erosion. Where the coating is sputtered away, the budding of new cones (figure 4) occurs. Thus the extended impurities does not seem to have any role in generating surface cones except to save them from destruction.

The overlying coating is clearly visible when the cones are viewed directly from overhead. Some typical micrographs are shown in figure 6. It is interesting to note that a number of cones have concentric rings of coatings separated by gaps. Rossnagel and Robinson (1981) found that the overlying covering extends to only the upper $3/4$ of the cone and tends to recede from the cone top as it grows, thereby developing a gap at the apex. While this is true for most of the cones, the formation of several gaps in the coating on some cones cannot be explained only by surface diffusion and direct deposition of impurities alone (Rossnagel and Robinson 1981). Moreover, in spite of the presence of coating, the upper portion of the cones also has a regular structure like the base, contradicting the observations of Rossnagel and Robinson (1981). Quite recently, Morishita and Okuyama (1990, 1991) studied seed cone formation on Cu substrates. They found that the impurities deposit epitaxially on the slopes of cones. In an early experiment, Erlenwein (1977, 1978) observed fine-scale ripple structures developed on the cone facets. It is generally concluded that this is associated with elaboration of the subsurface dislocation network that forms to relieve the stresses generated by ion-beam induced defects (Carter *et al* 1985). It therefore seems that the underlying crystalline structure of the cone material plays a part in the formation of ring-like morphologies on the cone surface. In passing, it may be mentioned that Morishita and Okuyama (1991) observed the big cones exclusively on the areas remote from the seed source where both the seed flux and the incident ion-flux are low. According to their hypothesis, the cone evolution is due to two competing effects, the ion-etching and the redeposition of sputtered atoms. They concluded that the growth of big cones is not due to the impurity effect but the result of relatively enhanced redeposition of sputtered target atoms. However, this mechanism of cone evolution is not well established so far.

3.2 Topography of the eroded Si samples

Here, the results of a typical etched surface for 1 h of bombardment are described. Scanning electron microscopy of the surface of the crater revealed mainly the development of etch pits (figure 7). Few conical structures were also found to appear, their number density being lower at higher etching time. Normally in crystalline materials,

Figure 6. Some electron micrographs showing the top view of cones with concentric rings of coatings on the surfaces. White markers = 1 μm .

Figure 7. Electron micrograph of the irradiated Si(111) surface showing etch pits and cones. The arrows indicate the cones with secondary pits. White markers = 10 μm .

pits are developed where the extended defects such as dislocations and stacking faults intersect the surface. Such defects may be considered to modify the surface atomic binding energy and thus modify the local sputtering yield. In the case of Si, a different mechanism of pit formation was put forward by Carter *et al* (1984). It was theorized that at the interface between the ion-induced amorphized Si layer and the underlying crystalline substrate, stresses are developed parallel to the surface by the collision cascade. This creates microcracks which are thought to be the precursors of pits. In passing, it should be noted that many workers (Carter 1984; Carter *et al* 1984; Duncan *et al* 1984; Chini *et al* 1991) reported terraced or corrugated structures on Si formed by the overlapping of etch pits when the surfaces are irradiated at oblique ion incidence. In the present experiment, the absence of such structures indicates a near-normal particle bombardment to the surface (Carter *et al* 1985). This is also supported by the fact that all the cones were seen to have their axes perpendicular to the specimen surface.

Detailed examination of the pits containing conical protrusions shows a second generation of pits developed around the cone bases. This is clearly discernible in the higher magnification micrographs (figure 8). The secondary pit is believed to be generated due to an enhanced erosion caused by the combined bombardment of the primary beam and secondary particles which are reflected and scattered from the cone's surface.

An early stage of the impurity induced cone development is the formation of an elevated mesa or plateau of the matrix material (Linders *et al* 1986). Figure 9 illustrates a typical mesa formation, while figure 10 shows the coexistence of a mesa and a well-defined cone. The impurity cap is plausibly composed of carbon particles synthesized from hydrocarbon molecules, since EDX analysis shows no signals of Ta. The reason might be that the sputtering yield of Ta is higher than that of Si (Andersen and Bay 1981), as a result of which Ta atoms cannot settle on the Si substrate during irradiation.

Figure 8. Higher magnification electron micrographs of a typical cone showing the development of groove or trench around the bottom of the cone standing on the primary pit; (a) tilt 45° and (b) tilt 0° . White markers = $1\ \mu\text{m}$.

An interesting observation is the development of dimeric cones and cluster of cones, some typical micrographs of which are shown in figures 11–13. Quite recently, Nindi and Stulik (1988) reported a similar phenomenon where a so-called supercone is formed by the fusion of several adjacent cones at high enough doses. It is speculated that the valleys between the cones are filled up by the redeposited sputtered materials from the neighbouring areas during proceeding bombardment. The present cones seem to be not due to redeposition effects. They are probably evolved as such from a group of impurity-induced mesas, which may be confirmed from figure 10.

Figure 9. Electron micrographs showing a typical mesa formation induced by contaminant protection. White markers = 10 μm .

Figure 10. Electron micrographs showing a conical structure and a mesa developed side by side; (a) tilt 45° and (b) tilt 0°. In the latter micrograph, the impurity cap on the mesa is clearly visible. White markers = 1 μm .

Figure 11. Electron micrograph showing a dimeric cone. Note that the underlying pit at the base also has a dimeric structure with the same symmetry as the cone. White markers = 1 μm.

Figure 12. Electron micrographs showing another dimeric cone; (a) tilt 45° and (b) tilt 0°. White markers = 10 μm.

Figure 13. Electron micrographs showing cluster of cones; (a) tilt 45° and (b) tilt 0° . White markers = $10\ \mu\text{m}$.

4. Conclusions

The modified surface topography of Cu and Si in PIG discharge is found to be quite similar to that obtained in well-defined bombardment conditions as reported in the literature (e.g. see Ghose and Karmohapatro 1990).

In the case of Cu, a high density of cones is found to develop on the sputtered surface. Several familiar characteristics such as the formation of trench at the base of the cone, faceting of cones and bending of cones are observed. The most striking feature is that a number of cones are coated with thin layers of impurity. Besides the impurity cap at the top of the cone, contours of equal thickness impurity layers resembling ring-like structures with some gaps in between are formed on the cone

surfaces. Such a decoration may be attributed partly to the underlying crystalline structure of the cone's surface. Since the coatings are visible on relatively big cones, this suggests that as a result of this coating the cones get the opportunity to grow in size under continued erosion.

In the case of Si, etch pits are mainly developed on the sputtered surface. A few conical protrusions are also formed; these are accompanied by shallow surface depressions in addition to the primary pits. The development of dimeric cones and cluster of cones seems to be not an effect of redeposition.

The present study reveals that Si is not as susceptible to cone formation as Cu. This indicates that the structural state of the target influences the type of the topographical features, as it is well-known that the surface of Si tends to become amorphous under ion bombardment. Finally, this study also shows that etching in a PIG discharge is very efficient in producing a Cu surface with a large population of well-defined cones which may be utilized as a selective absorbing surface in solar thermal collectors or in other applications as discussed by Auciello (1981).

Acknowledgements

The authors thank Prof. Dr E Salzborn of the University of Giessen, Germany for a gift of the PIG ion source. Thanks are due to RSIC, Calcutta, TIFR, Bombay and IIT, Kharagpur for SEM work. The authors also thank I Das for help in EDX measurements.

References

- Alexander V, Lippold H -J and Niedrig H 1981 *Radiat. Eff.* **56** 241
- Andersen H H and Bay H L 1981 in *Sputtering by particle bombardment I* (ed.) R Behrisch (Berlin: Springer Verlag) p. 145
- Auciello O 1981 *J. Vac. Sci. Technol.* **19** 841
- Baumann H and Bethge K 1974 *Nucl. Instrum. Meth.* **122** 517
- Berg R S and Kominiak G J 1976 *J. Vac. Sci. Technol.* **13** 403
- Carter G 1984 *Vacuum* **34** 819
- Carter G, Lewis G W, Nobes M J, Cox J and Begemann W 1984 *Vacuum* **34** 445
- Carter G, Nobes M J and Whitton J L 1985 *Appl. Phys.* **A38** 77
- Chini T K, Bhattacharyya S R, Ghose D and Basu D 1991 *Jpn. J. Appl. Phys.* **30** 2895
- Duncan S, Smith R, Sykes D E and Walls J M 1984 *Vacuum* **34** 145
- Erlenwein P 1977 *Untersuchungen zum Einfluß der temperatur und der kristallinen struktur von Einkristallen auf die anisotrope Emission bei 8keV Ar-Ionenbeschuß*, Thesis D 83, Technical University of Berlin, Germany
- Erlenwein P 1978 *Phys. Status Solidi (a)* **47** K9
- Ghose D and Karmohapatro S B 1990 in *Advances in electronics and electron physics* (ed.) P W Hawkes (New York: Academic Press) Vol. 79, p. 73
- Kelly R and Auciello O 1980 *Surf. Sci.* **100** 135
- Linders J, Niedrig H, Ram N and Koch H 1986 *Radiat. Eff.* **88** 105
- Morishita S and Okuyama F 1990 *J. Vac. Sci. Technol.* **A8** 3295
- Morishita S and Okuyama F 1991 *J. Vac. Sci. Technol.* **A9** 331
- Nindi M and Stulik D 1988 *Vacuum* **38** 1071
- Robinson R S and Rossnagel S M 1982 *J. Vac. Sci. Technol.* **21** 790
- Rossnagel S M and Robinson R S 1981 *Radiat. Eff. Lett.* **58** 11
- Rossnagel S M and Robinson R S 1982 *J. Vac. Sci. Technol.* **20** 506
- Sen A K and Ghose D 1991 in *Fifth National Symposium on Mass spectrometry preprint volume* (Indian Society for Mass Spectrometry) Paper No AMP 1
- Wehner G K and Hajicek D J 1971 *J. Appl. Phys.* **42** 1145
- Wehner G K 1985 *J. Vac. Sci. Technol.* **A3** 1821
- Whitton J L, Kiriakidis G, Carter G, Lewis G W and Nobes M J 1984 *Nucl. Instrum. Meth.* **B2** 640