Copper surface morphology developed in a magnetron sputtering system

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A study has been made of the effects of ion bombardment on copper surface morphology in a magnetron sputtering system using different glow discharge atmospheres of Ar, Ar/O_2 and Ar/N_2, respectively. The morphological features detected by the scanning electron microscope were: conical protrusions, etch pits, ripple and pillar structures. Conditions of cone formation were examined under the effects of: (1) ion dose, (2) gas type/content and (3) bombarding time. The results showed that treating copper in a mixture of (25% O_2 + 75% Ar) d.c. glow discharge produced a surface of a high population of well-defined cones which may be utilized as a selective absorbing surface in solar thermal collectors or in other applications.

1. Introduction

In recent years, there has been a growing interest in the study of ion bombardment of solid surfaces and numerous experimental [1–7] and theoretical [8–12] studies have been carried out to investigate the development of surface topographies particularly the formation of cones on ion-bombarded amorphous and crystalline targets.

These studies have shown an increasing range of some possible applications of these textured surfaces, namely

(a) a dense conical array appears to be a desirable surface structure [7, 13, 14] for the inner walls of nuclear fusion devices;

(b) surfaces with a needle-like structure have proved to be good absorbers for solar energy conversion technology [15, 16];

(c) coned surfaces were found to be of interest for application as solar selective absorbers particularly in solar thermal collectors [17, 18];

(d) it was found recently [19] that, certain molecules absorbed on some rough (coned) surfaces, e.g. copper, silver and gold, showed an enhanced Raman scattering effect 10^4 to 10^6 times larger than that observed from scattering on the same molecule in a free state; and

(e) other technologies.

Arising from these findings, it was considered useful to substantiate earlier studies and throw more light on the surface behaviour of polycrystalline copper in different glow discharge treatments in a trial to produce a surface of a high population of well-defined cones which may be utilized as a selective absorbing surface in the solar thermal collectors or in other applications.

2. Apparatus and method

The arrangement of the d.c. planar magnetron sputtering system used in this study was given elsewhere [20]. A copper disc (99.9% purity) was clamped and rested on the water-cooled electrode and during sputtering a circular erosion track was formed on its surface with a mean diameter of 35 mm and a track width of 12 mm.

To study the effects of sputter-etching on copper surface morphology, specimens ($\frac{1}{2} \times 1\frac{1}{2}$ cm) of purity 99.9% were cut and placed on the copper disc (using a circular clamp) so that the specimens were subjected to the ionic bombardment in the erosion track.

High-purity argon gas (99.999%) supplied by EIAG (Cairo, Egypt), was used in some experiments while in other experiments argon was premixed with either oxygen or nitrogen (both were of the same purity of argon) and passed through a liquid nitrogen trap via a needle valve to the chamber. The liquid nitrogen trap was used to reduce the partial pressure of the condensable gas in the discharge atmosphere which was generally assumed to be chiefly water vapour.

All experiments were made at a constant chamber pressure of 10^{-1} mbar, and scanning electron microscopy was used to examine the changes in surface morphology before and after bombardment in the different plasma atmospheres.

3. Experimental results

Before treating the copper samples in the different glow discharges, the samples were first electrochemically polished. The appearance of the surface after polishing is shown in Fig. 1 where it is clear that the surface is flat and smooth except for some irregularities and dust particles left on the surface probably due to the polishing procedure.

The different glow discharge treatments used in this investigation and the various morphological features obtained on the treated copper samples are given below.

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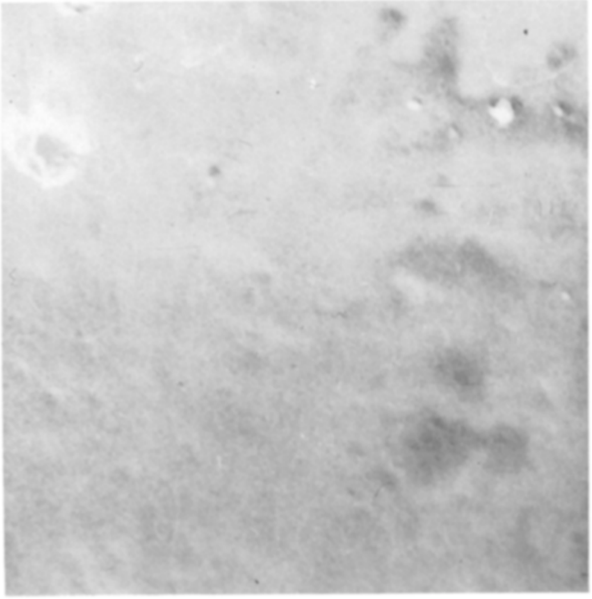

Figure 1 Appearance of a polished copper sample before bombardment, × 1000.

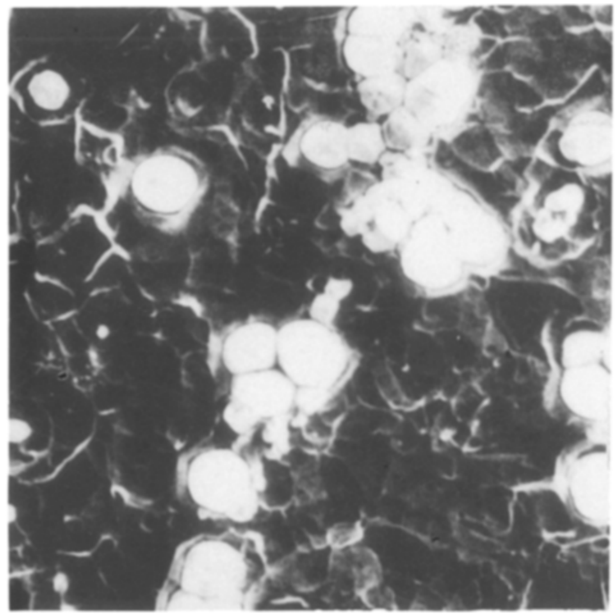

Figure 3 A copper sample after 2 h bombardment in argon glow discharge, × 1000.

3.1. Treatment in argon d.c. glow discharge

Argon ion bombardment of the polished copper samples with 225 V and a current density of $6\,\mathrm{mA\,cm^{-2}}$ (ion dose of $4.1 \times 10^{17}\,\mathrm{cm^{-2}}$) resulted in the formation of the following morphological features as can be seen in Figs 2 to 4.

Fig. 2 shows the effects of the ionic bombardment on the copper surface morphology after 1 h. It can be seen that this bombardment produced an irregular surface associated with the appearance of cones and etch pits. The upper left corner of this figure shows the presence of a deformed (slipped) cone.

On increasing the period of bombardment to 2 h, the surface became deeply eroded (Fig. 3). The etch pits became more visible all over the surface and the interior of cavities can now be observed. The cones shown in Fig. 2 were largely eroded and became approximately level with the surface.

Fig. 4 is a higher magnification of Fig. 3 and shows some eroded cones together with their surrounding etch pits. It is of interest to notice that one of these cones (A) was eroded more than the others (B, C and D) and as a result the interior of its surrounding etch pit can now be clearly observed.

3.2. Treatment in a gaseous mixture of (25% O_2 + 75% Ar) d.c. glow discharge

Using a gaseous mixture of 25% O_2 + 75% Ar instead of pure argon in the d.c. glow discharge resulted in the formation of more features on examination by scanning electron microscopy and as shown in Figs 5 to 7.

Fig. 5 shows the effects of the co-sputter etching mechanism on the copper surface morphology after 1 h treatment. In this figure, broadened grain boundaries were observed and the grains started to form a

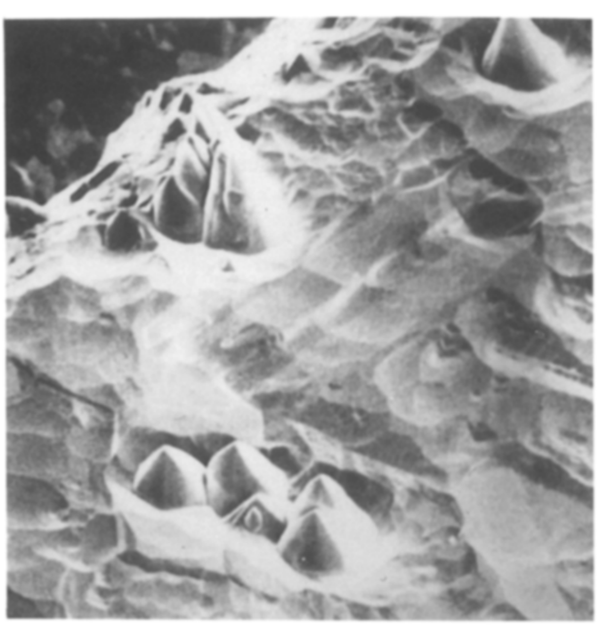

Figure 2 A copper sample after 1 h bombardment in argon glow discharge, × 1000.

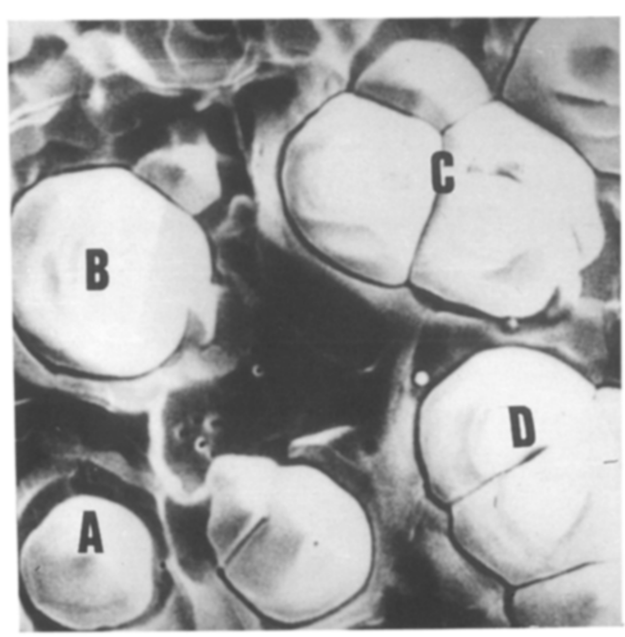

Figure 4 Appearance of the copper sample after 2 h bombardment in argon glow discharge, × 2500.

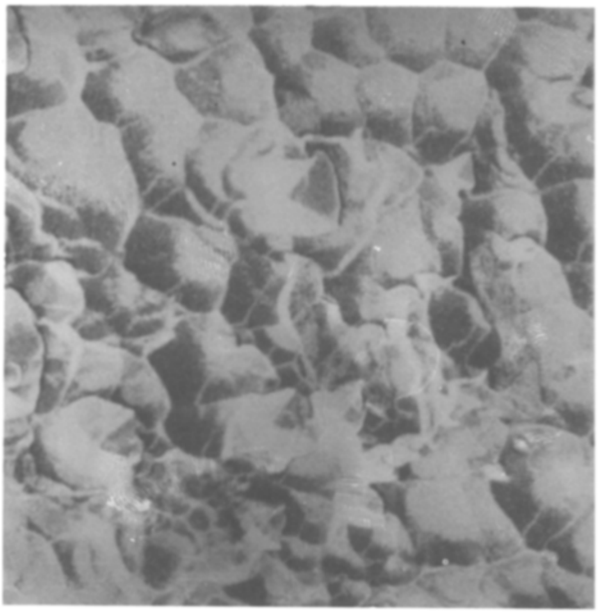

Figure 5 The hexagonal pillar structure formed after 1 h bombardment in (25% O_2 + 75% Ar) glow discharge, ×2500.

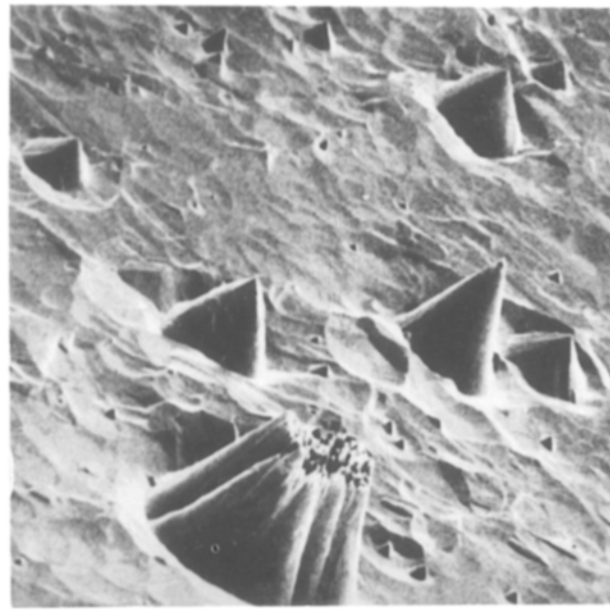

Figure 7 Different isolated cones developed after 2 h treatment in (25% O_2 + 75% Ar) glow discharge, ×1000, 50° tilt.

hexagonal pillar structure. The pillar structure obtained has given the chance for initiation and growth of the fine cones observed in Figs 6 and 7, respectively, after 2 h treatment. The cones observed in Fig. 7 were of different heights and basal areas.

The values of voltage and current density used were 225 V and 9.1 mA cm^{-2} (ion dose of 6.25×10^{17} cm^{-2}).

3.3. Treatment in a gaseous mixture of (50% O_2 + 50% Ar) d.c. glow discharge

Increasing the oxygen content in the glow discharge from 25% to 50% reduced the surface erosion, as can be seen clearly in Figs 8 to 10.

Treating the copper sample for 1 h produced many small protrusions on the surface with the formation of a porous layer which is believed to be copper oxide, Fig. 8. The structures of these protrusions are shown in Fig. 9 and are found to be different from that obtained previously for the fine cones formed when using either argon or 25% O_2 + 75% Ar d.c. glow discharges.

Prolonged treatment of the sample (2 h) produced a cone-free surface covered with a thicker layer of copper oxide, Fig. 10. The isolated protrusion observed in the last figure was the only one detected over the entire surface of the treated sample.

The values of voltage and current density used in this experiment were 225 V and 6.4 mA cm^{-2} (ion dose of 4.4×10^{17} cm^{-2}).

3.4. Treatment in a gaseous mixture of (25% N_2 + 75% Ar) d.c. glow discharge

When nitrogen was added to the argon gas to form a mixture of 25% N_2 + 75% Ar, copper samples treated

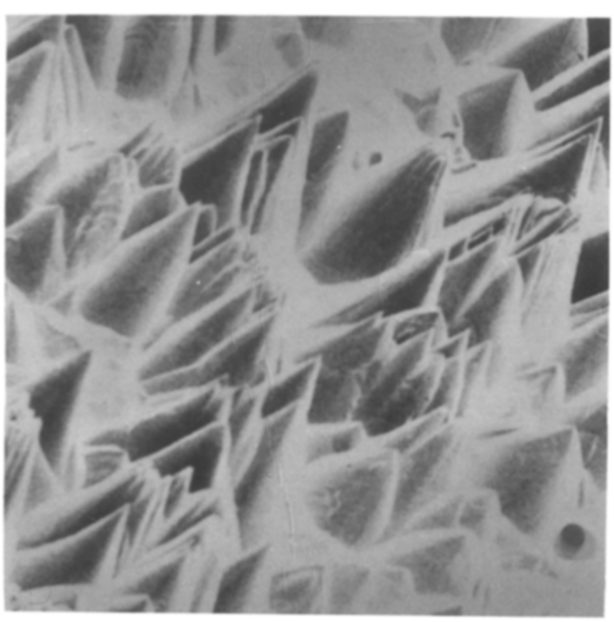

Figure 6 A high population of well-defined cones after 2 h treatment in (25% O_2 + 75% Ar) glow discharge, ×1000, 50° tilt.

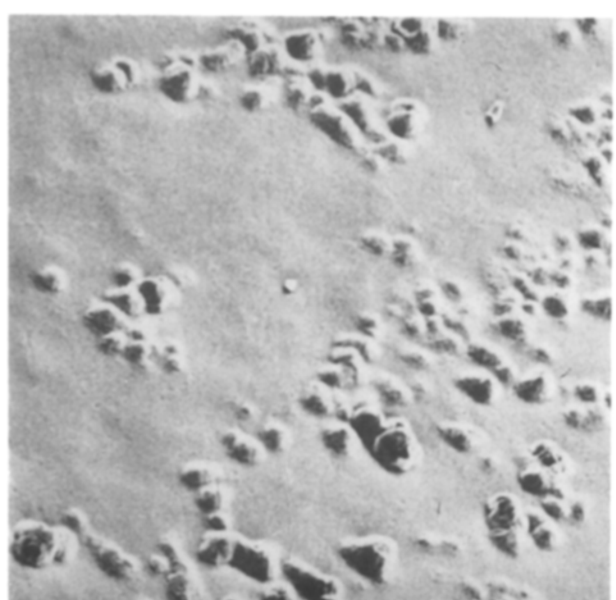

Figure 8 Appearance of the polished copper surface after 1 h treatment in (50% O_2 + 50% Ar) glow discharge, ×1000.

Figure 9 Structures of conical protrusions observed after 1 h treatment in (50% O_2 + 50% Ar) glow discharge, ×2500.

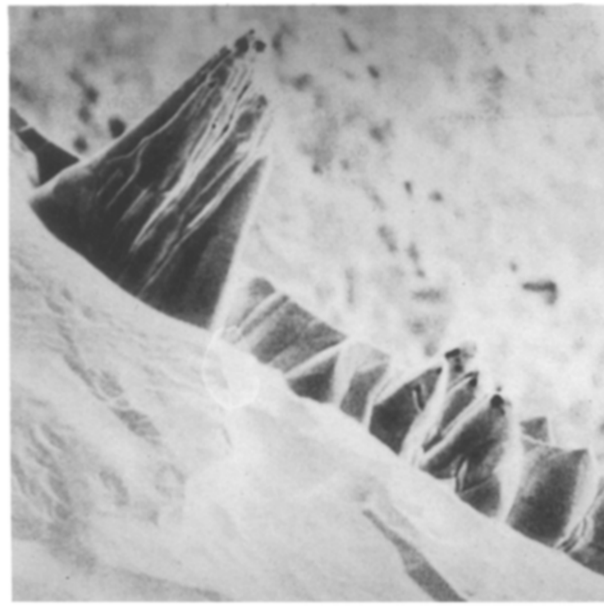

Figure 11 Cone formation along a deep cavity and the appearance of the ripple structure after $\frac{1}{2}$ h in (25% N_2 + 75% Ar) glow discharge, ×2500, 50° tilt.

in this discharge for $\frac{1}{2}$ h with 225 V and a current density of 5.5 mA cm^{-2} (ion dose of 3.75×10^{17} cm^{-2}) showed a slightly eroded surface associated with the formation of cones and a ripple structure (wave-like structure) as shown in Figs 11 and 12.

Fig. 11 shows the formation of some cones of different heights distributed along a deep cavity while Fig. 12 shows the appearance of only one isolated cone found in another zone on the same treated sample.

Increasing the periods of treatment to 1 and 2 h, respectively, the samples showed more surface erosion with the formation of many conical protrusions as shown in Figs 13 and 14. The dimensions of these protrusions (height and basal area) were found to increase significantly with time.

4. Discussion

The micrographs show the formation of some morphological features distributed over the surfaces of the copper samples as a result of treatment in the different glow discharges mentioned above. The morphological features observed in this experimental work are: (1) surface erosion and surface evolution; (2) formation of cones; (3) formation of a pillar structure; and finally, (4) formation of a ripple morphology (wave-like structure).

The different mechanisms associated with the above-mentioned features are discussed below.

4.1. Surface erosion and surface evolution

From the different micrographs it can be seen that

Figure 10 The cone-free surface appearing after 2 h treatment in (50% O_2 + 50% Ar) glow discharge, ×1000.

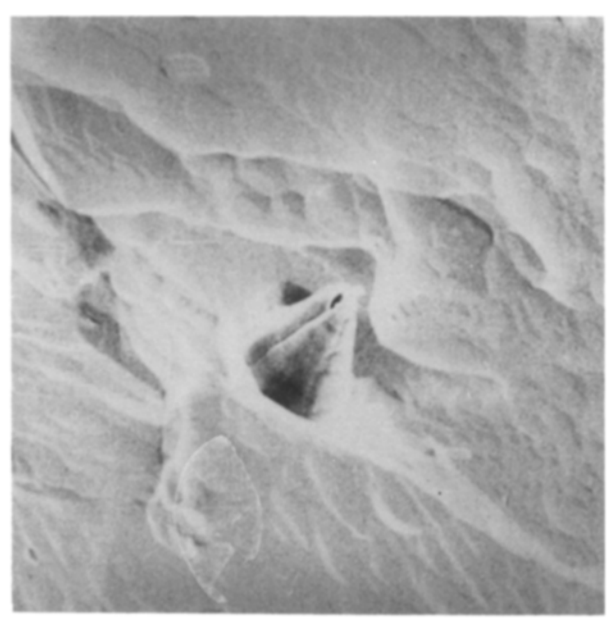

Figure 12 An isolated cone developed after $\frac{1}{2}$ h in (25% N_2 + 75% Ar) glow discharge, ×2500, 50° tilt.

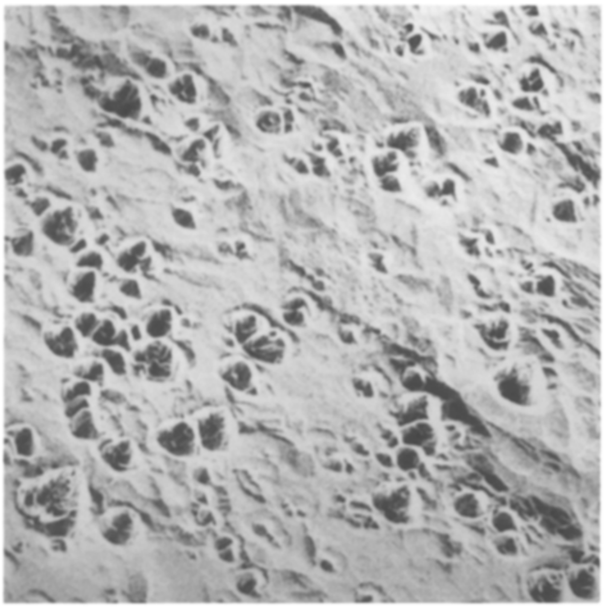

Figure 13 Conical protrusions after 1 h bombardment in (25% N_2 + 75% Ar) glow discharge, ×1000.

Figure 14 Large cones observed after 2 h in (25% N_2 + 75% Ar) glow discharge, ×1000.

polished surfaces of the copper samples were greatly eroded due to ionic bombardment in the different glow discharges. Surface evolution due to a prolonged period of ionic bombardment was also critically observed in the same micrographs.

Table I lists all morphological features which appeared on copper surfaces as a result of increasing treatment time and changing gas atmosphere.

Table I reveals that the erosion behaviour of copper in argon is entirely different to that resulting when using 25% O_2 + 75% Ar glow discharge. In other words, treating the sample for 1 h in argon resulted in the formation of some conical features (Fig. 2), while if the sample was treated for the same period of time in 25% O_2 + 75% Ar, an increased selective sputtering at the grain boundaries was observed with the formation of what is called a pillar structure (Fig. 5).

On increasing the bombarding time to 2 h, the sample treated in argon revealed eroded cones and deep cavities (Fig. 3), while that treated for the same period in 25% O_2 + 75% Ar showed a surface of a high population of well-defined cones as shown in Fig. 6. This behaviour was previously obtained by Rizk [4] in his work on stainless steel where it was found that surface roughness as measured by the talysurf was of a fluctuating character with bombarding time, and that the erosion behaviour in argon and Ar/O_2 glow discharges were of an opposing manner to each other (Fig. 15).

On increasing the oxygen content in the discharge to 50% instead of 25%, the surface revealed no morphological features even after 2 h treatment (Fig. 10). This is to be expected, because the metal oxide formed partially dissipates the ion impact energy by oxide dissociation.

A possible explanation for the overall surface evolution can be given. The polishing procedure tends to produce surface irregularities and/or impurities which interfere with the uniformity of the sputtering process in two ways: (a) primary effects [10, 21, 22] – due to the change of sputtering rate with angle of incidence to the surface normal, so that the irregular surface develops a steeper profile; (b) secondary effects [1, 23, 24] – scattered ions, reflected ions and high-energy sputtered atoms from the edge of surface irregularities can enhance the sputtering at the bottom. As a result, the irregularities tend to become better defined and with a groove around them. This is shown clearly in Figs 2 and 4 to 7.

4.2. Formation of cones

The formation of cones on solid surfaces with ions has

TABLE I

Gas content	Ion dose (10^{17} cm^{-2})	Surface evolution				Surface erosion: Degree of surface erosion
		Features after 1 h treatment	Fig. no.	Features after 2 h treatment	Fig. no.	
25% O_2 + 75% Ar	6.2	Pillar structure	5	Very densely coned surface	6	Very high
100% Ar	4.1	Cones + etch pits	2	Eroded cones + cavities	3	High
25% N_2 + 75% Ar	3.75	Small protrusions	13	Large cones	14	Moderate
50% O_2 + 50% Ar	4.4	Small protrusions + copper oxide	8	Cone-free surface + a thicker film of copper oxide	10	Nil

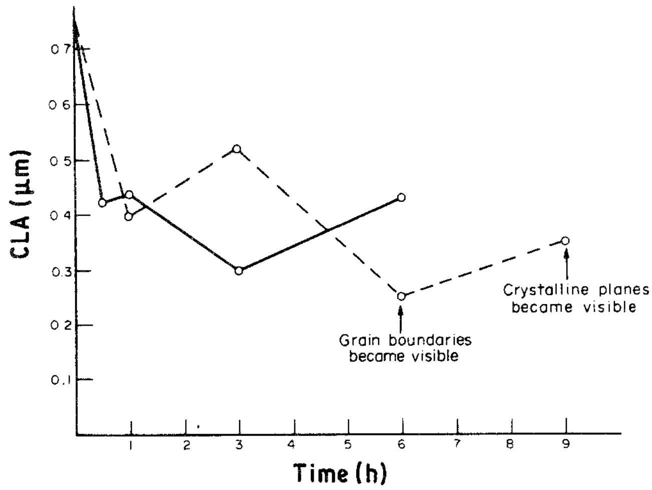

Figure 15 Centre-line average after different treatment periods in (– – –) argon and (——) Ar/O_2 glow discharges [4].

recently been reported by several workers [1–7]. Two mechanisms have been proposed to explain this phenomenon: (a) the partial masking mechanism [1, 8]; (b) the bombardment-induced defect mechanism [3, 25].

The results obtained in this study were found to support these two mechanisms and are discussed below.

4.2.1. The partial masking mechanism

The appearance of submicroscopic cones on glow discharge cathodes of various polycrystalline materials was first reported by Guntherschulze and Tollmien [26]. They postulated that the presence of particles with lower sputtering yields than their surroundings on the cathode surface would cause the growth of such cones.

The copper samples used in this study were of 99.9% purity, therefore the possibility that the above mentioned mechanism was in progress and took part in the formation of some of the cones observed in the different micrographs must be considered. We suggest that, initial thicknesses and basal areas of the masking particles on the bombarded surfaces are the main reasons for cone formation of different dimensions. The smaller the thicknesses and basal areas of these particles, the more rapid is the shrinkage rate of the cones. When the masking particles are thick and of large basal areas, the rate of shrinkage is relatively slow.

4.2.2. The bombardment-induced defect mechanism

In the partial masking mechanism, the presence of both impurities and foreign particles was considered to be a necessary condition for the formation of cones on sputtered targets. In the present study, some scanning electron micrographs have revealed other features which cannot be interpreted according to the assumptions made for the partial masking mechanism. These features are:

1. the formation of a hexagonal pillar structure (Fig. 5) followed by the formation of the well-defined cones shown in Fig. 6. The formation of these features can be attributed to the increased selective sputtering at the grain boundaries (zones of large strains) due to the high dose of ions used, leading to the formation of the pillar structure after 1 h treatment. The structure obtained had inclined edges on which bombarding ions were incident at different angles, therefore due to this and to the change of sputtering rate with angle of incidence to the surface normal, this structure was largely eroded with time and took the shape of the well-defined cones seen in Figs 6 and 7;

2. the formation of cones along the deep cavity shown in Fig. 11 as a result of the ion bombardment in 25% N_2 + 75% Ar glow discharge for $\frac{1}{2}$ h, can be attributed to the following assumption: ionic bombardment induced a dislocation network of a large strain which was selectively sputtered and formed the observed deep cavity. This assumption is supported by the presence of a ripple structure near to the cavity observed. Mazey and colleagues [27, 28] have suggested that a fine ripple structure can be directly associated with the bombardment-induced dislocation network.

Different depths inside the cavity were believed to be responsible for the formation of the different dimensions of the observed cones.

These results can substantiate those of earlier studies in which cone formation was attributed to the presence of bombardment-induced defects as well as to the partial masking mechanism.

5. Conclusion

Among the different treatments used in this study to reveal the surface structure of polycrystalline copper, the 25% O_2 + 75% Ar d.c. glow discharge was found to be very efficient in producing a surface of a high population of well-defined cones which may be utilized as a selective absorbing surface in solar thermal collectors or in other applications.

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