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ION BOMBARDMENT INDUCED CONE FORMATION ON GLASSY CARBON AND GRAPHITE SURFACES

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Abstract—Surfaces of various types of carbon were bombarded with 750 eV argon ions at low pressures to a total ion dosage of about 10^{20} ions/cm^2. This dosage was sufficient to produce distinctive conical protrusions at the surfaces of all samples. The study shows that sputtering is an effective way to roughen carbon surfaces.

1. INTRODUCTION

Surface topography changes due to ion bombardment are the basis for a number of materials applications involving optical absorption[1, 2], surface analysis[3, 4], nuclear reactor walls[5], biological implants[6], and adhesive bonding[7]. Although not yet described in the literature, a highly textured carbon or graphite surface should lead to good metal contact bonding. As a first step in exploring this potential application, ion bombardment induced surface topography was examined for a number of different glassy carbons and graphites.

During the ion bombardment of plane solid surfaces, cones, hillocks, facets, pyramids, pillar and cellular structures, shallow depressions and ripple structures have all been observed[8]. Cone formation, the most common microstructural occurrence, develops in both crystalline and amorphous materials. The mechanisms of such topography development are generally complex and can include such factors as [8–21]: dependence of sputtering yield on angle of ion incidence; type, energy and fluence of bombarding species; temperature of bombarded material; ion reflection; re-deposition; gaseous contamination; impurities; surface diffusion; nonuniform or multiphasic starting material; and micron-sized foreign particles on surface. In particular, Kaufman and Robinson[9] have recently determined the critical size of the contaminant cluster and also established the existence of a critical minimum temperature for cone formation. The angle between the cone surface and the normal is generally close to the maximum in sputtering yield vs angle of incidence[10].

The total ion dose appears to be the best parameter for classifying bombardment surface damage[8]. At about 10^{11} to 10^{15} ions/cm^2 submicroscopic nonuniformities nucleate. From 10^{15} to 10^{18} ions/cm^2 the nucleated nonuniformities (both compositional and structural) just begin to be observable microscopically and from 10^{17} to 10^{19} ions/cm^2 reach an equilibrium morphology. In the case of graphite, bombardment-induced damage becomes noticeable at 2×10^{17} ions/cm^2 and reaches an equilibrium surface structure (with dimensions on the order of several micrometers) at about 2×10^{18} ions/cm^2[8].

2. EXPERIMENTAL

The various glassy carbons and graphites were sputter-etched in an MRC Model SES 8632 *rf*-sputtering system by resting them on a 12.7 cm dia. water cooled cathode which is in the bottom of the system. The aluminum cathode was covered with a 12.7 cm dia. piece of Grafoil in order to prevent contamination. The sputter-etching conditions were: pumped to 26 μPa over 12 hr period; pure Ar at 0.66 Pa; *rf*-voltage = 750 eV; *rf*-power = 125 W; time = 24 hr. The total gas pressure was kept as low as possible so as to minimize any gas phase scattering and resulting re-deposition. The various bombarded target materials included three related glassy carbon samples which differed in their final HTT (1000, 2000 and 3000°C, respectively) anf four forms of graphite. The latter included stress recrystallized graphite, Grafoil, a cold-pressed pellet of SP-1 natural graphite and polycrystalline graphite.

3. RESULTS AND DISCUSSION

For the total ion dosage used in this experiment (about 10^{20} ions/cm^2), it is expected that the bombardment-induced topographical features should be at a steady state. As seen in all the figures, conical protrusions are well developed on all the various forms of carbon and graphite. There are, however, some material-dependent differences in the cone formations which will be described below.

For the three glassy carbon samples, the largest changes are seen. The fractured surfaces of the unbombarded samples (Fig. 1a–c) show, first, a distinct increase in density and surface smoothness with increasing HTT and, second, some micrometer-size debris covering about 5% of the surface. The latter is apparently the result of the pre-deposition fracturing procedure and is not expected to have a significant effect on the overall surface features due to their small percent coverage. The corresponding conical features due to ion bombardment (Fig. 1d–f) show a decrease in size with increasing HTT temperature. The higher magnification of a portion of Figs. 1d and 1f (Figs. 2a, b, respectively) shows that the smaller cones (Fig. 2b) are individual

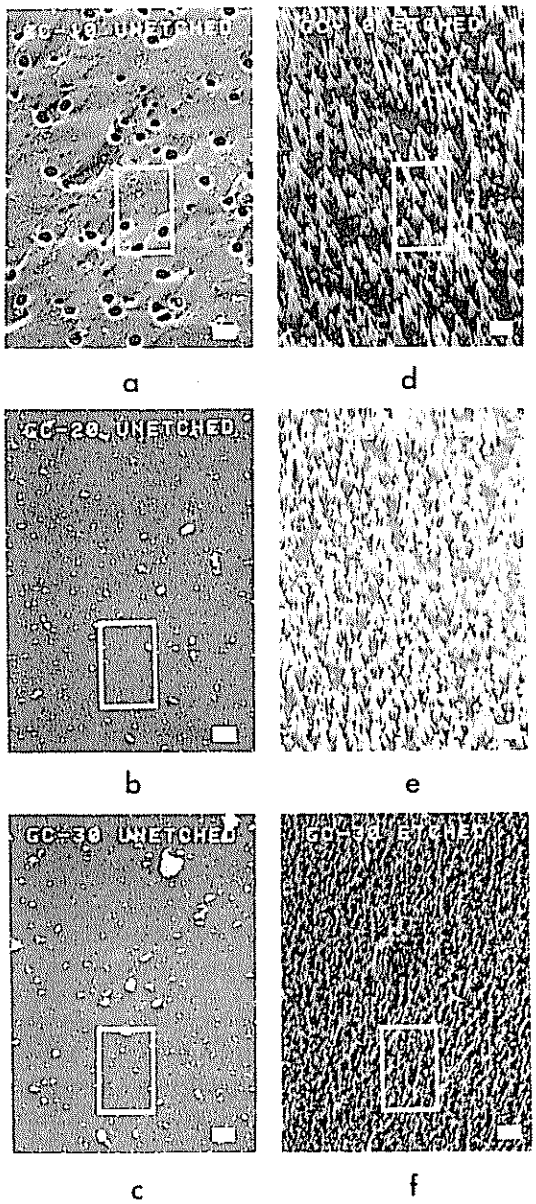


Fig. 1. SEM micrographs of thres glassy carbons both before (a–c) and after (d–f) sputter-etching. HTT were: (a and d) 1000°C; (b and e) 2000°C; and (c and f) 3000°C. The surfaces studied were fractured with one side sputter-etched and the other untreated. The white marker represents 10 μm.

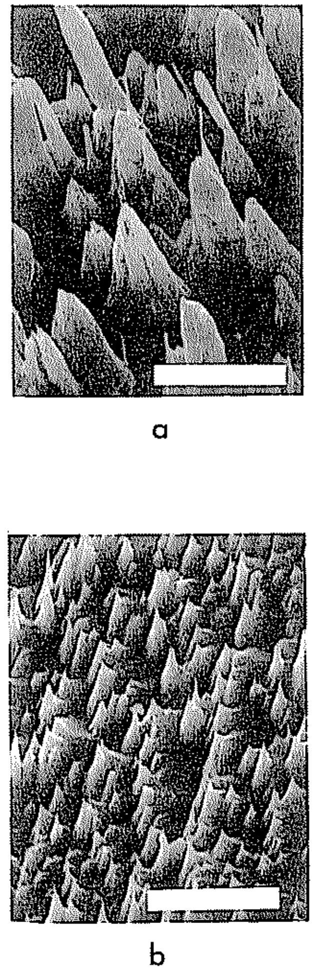
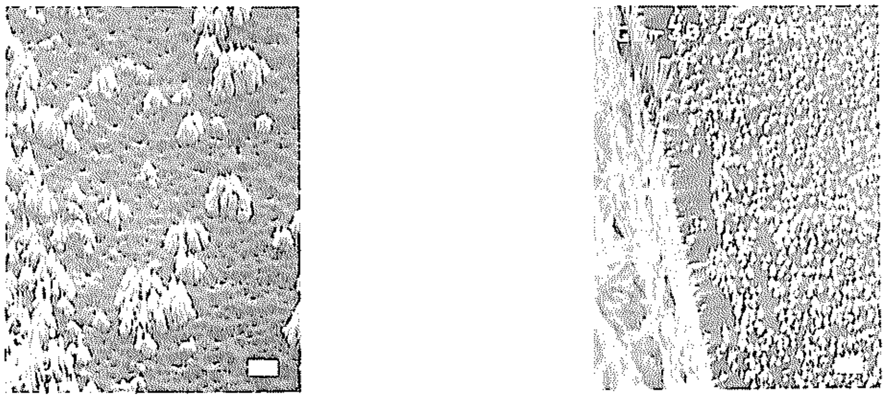


Fig. 2. Higher magnifications of surface features seen in Fig. 1 for (a) 1000°C and (b) 3000°C samples after bombardment. SEM micrographs correspond to the area within the rectangular boxes in Fig. 1d, f, respectively.

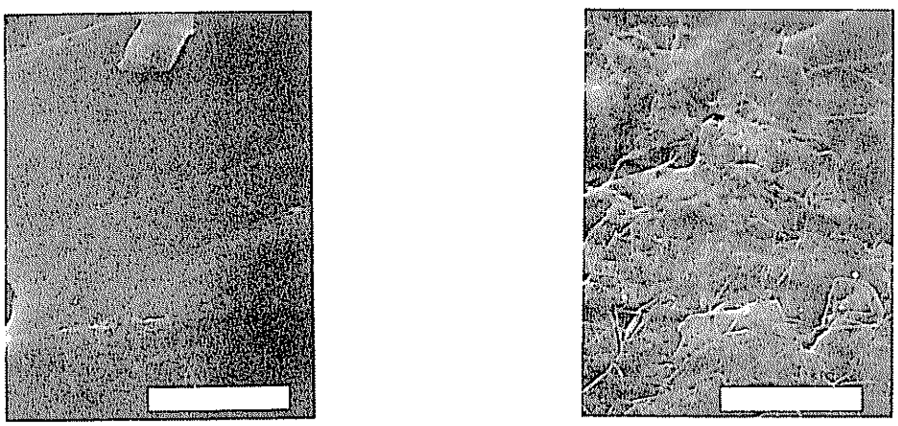
cones while the larger cones (Fig. 2a) are actually a cluster of smaller cones, all pointing toward the same apex and having about the same side angle as the smaller, individual cones. Also, the total density of cones and total surface coverage by cones increase with increasing HTT of the glassy carbon. Finally, near the edges of the samples, where higher bombardment rates are expected due to flux enhancement, the density of cones decreases (Fig. 3), while the size remains about the same (compare Figs. 1 and 3). Again, clustering of smaller cones to make larger cones is seen only for the lower HTT material (Fig. 3a). Also, the areas with no cones are smooth in Fig. 3(b), while shallow depressions with sizes similar to the clustered conical bases are seen in Fig. 3(a). Additionally, it is noted that the holes, present in both the etched and unetched materials, occur at the bottoms of these shallow depressions. Since shallow depressions have been shown to result from the initial evolution and receding of cones [12], the cluster cones may have their origin, at least in part, at or near these ~ 1 μm-sized void areas.

Despite the wide diversity, both compositionally and structurally, of the various forms of graphite investigated (see Fig. 4—d), the resulting conical structures due to ion bombardment are all similar in both size and density (see Fig. 4e–h). The tallest cones, which are the most noticeable in the micrographs, appear to be clusters of cones similar to those found in the lowest HTT glassy carbons. These cluster cones are clearly seen in Fig. 4(g) where the cluster density is the smallest. It is interesting that the roughest initial surface (polycrystalline graphite, Fig. 4d) has the most uniform conical array pattern (Fig. 4h). This perhaps indicates that ion bombardment affects the

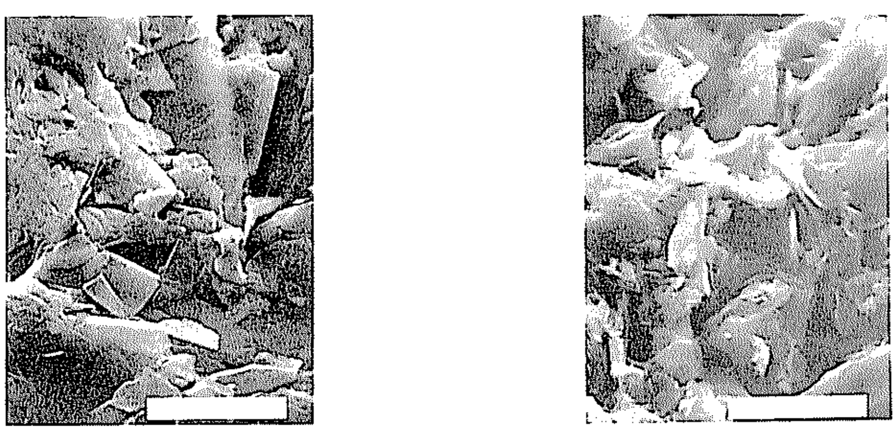


3(a) 3(b)

Fig. 3. Surface areas near the edges of (a) 2000°C and (b) 3000°C samples after bombardment.

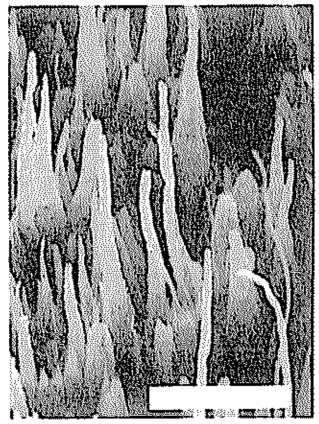


4(a) 4(b)

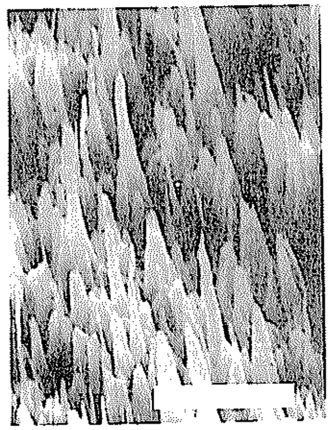


4(c) 4(d)

Fig. 4. SEM micrographs of four different forms of graphite both before (a–d) and after (e–h) sputter-etching: (a and e) stress recrystalized graphite; (b and f) Grafoil; (c and g) cold pressed pellet of SP-1 graphite; and (d and h) polycrystalline graphite.

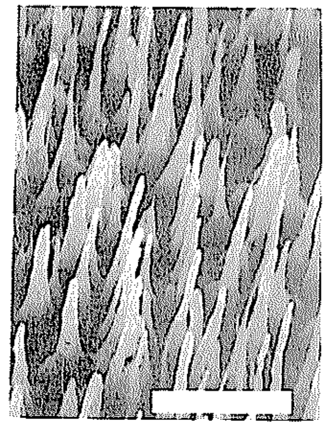


4(e)



4(f)

4(g)



4(h)

top and subsurface layers sufficiently that cone formation is more a function of the type and energy of bombarding species than the initial state of the surface. Also, the effect of direct re-deposition at the base of non-normal surfaces will be to smoothen the surface. Thus, the overall uniformity of the cones seems to mimic only the surface features which are much larger than the cone dimensions (compare the unetched and etched surface structures in Fig. 4).

For the ion bombardment conditions used in this experiment, a high density of cones resulted for all the various carbon target materials. Both their high density and the presence of tall cones indicate that the cones do not recede to any significant degree, such as those due to debris or surface contamination[12]. Also since the various carbons represent a wide range of chemical purities and chemical uniformities, the cone formation is not likely linked simply to such chemical effects. Thus cone formation seems to be an intrinsic property of carbon, albeit altered by the ion bombardment induced surface and sub-surface damage. Systematic changes were seen for the well-defined set of glassy carbons, indicating that some type of second phase formation, such as diffused impurities or inclusions or holes, controls the resulting cone formations through cone clustering. For the various graphites, however, no such changes were seen, with cone clustering seen in all cases.

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