JOURNAL OF MATERIALS SCIENCE 27 (1992) 553–556

Adhesion improvement in diamond films by microlithographic patterning

J. F. DENATALE, J. F. FLINTOFF, A. B. HARKER
Rockwell International Science Center, Thousand Oaks, CA 91360, USA

The use of microlithographic surface patterning has been investigated as a means of modifying the nucleation and adhesion of diamond films on non-compatible substrates. Significant improvements in film adhesion were achieved using this technique, to the point that interfacial integrity was maintained even at stress levels which induced subsurface fracture in the supporting substrate.

1. Introduction

The recent advances in the low-pressure synthesis of diamond thin films have the potential to impact numerous technologies due to diamond's unique combination of optical, mechanical, and electrical properties. Formation of these films from hydrogen–hydrocarbon gas mixtures has been demonstrated by a variety of techniques including hot filaments, microwave plasmas, and high velocity torches [1]. The vast majority of the work described in the literature documents growth and characterization of diamond films on Si and carbide forming metallic substrates due to the relative ease of growth and adherence to these materials. On many substrate materials, however, the diamond films tend to exhibit poor adherence, and typically disbond at thicknesses of the order of a few micrometres due to the development of intrinsic growth and thermal mismatch stresses. To fully exploit the potential of the diamond films, fabrication on less-compatible substrates must be addressed. One approach investigated in this work has been the use of microlithographic patterning of the substrate surface prior to film deposition in order to improve film adhesion. The surface patterning provides an increased surface area for bonding, enhances film uniformity [2] and, if the pattern is undercut, offers a means of physically "locking" the film onto the substrate. This approach has been found to significantly improve film adhesion.

2. Experimental procedure

Fused silica windows were patterned by standard photolithography and dry etching techniques prior to film growth. This produced grid patterns of 1 μm wide etched lines separated by 10 μm square spaces of unetched silica and 3 μm lines separated by 15 μm. The depths of the etched lines were approximately 1 μm in all cases. Processing conditions that gave both sharp sided and rounded etch profiles, respectively, (Fig. 1) were used to determine the effects of profile geometry on film adhesion. Diamond films were deposited using microwave plasma CVD with a source gas composition of 0.5% CH_4, 0.2% O_2, and the balance H_2. Substrate growth temperatures of 750 °C were used as determined by optical pyrometry. Unpatterned substrates were also included in the depositions for experimental comparison. All substrates were prepared using identical diamond polish pretreatments to enhance film nucleation.

3. Results

In the initial experiment, after approximately 16 h of growth local film delamination was observed on the unpatterned substrate, so no further film growth was conducted on this substrate. The patterned substrate with the rounded etch profile exhibited local film adhesion, although much of the film had already disbonded. The films on the substrates patterned with sharp etch profiles, however, maintained their integrity, demonstrating an improvement in adhesion associated with the patterning. The diamond film surfaces were characterized by highly faceted grains approximately 1 to 2 μm in size.

Diamond growth was continued on these substrates, and even after a film thickness of 9 μm, the topology of the initial pattern was still clearly evident in the film (Fig. 2). Subsequent tests showed evidence of the pattern to persist to film thicknesses of over 24 μm. By this thickness, cracks had become apparent in the film (Fig. 2). Cross-sectional SEM revealed, however, that these were not the result of film delamination. Rather, the stresses generated by the growing film and the high temperature processing induced subsurface fracture in the silica substrate itself (Fig. 3). The integrity of the film–substrate interface was still maintained even after the substrate fracture. These micrographs further indicated a strongly columnar grain structure, with the etched lines characterized by slightly inward sloping sides.

A filamentary structure was observed in the regions of the cracks (Fig. 4). This is attributed to H_2 etching of the SiO_2 substrate and the subsequent redeposition

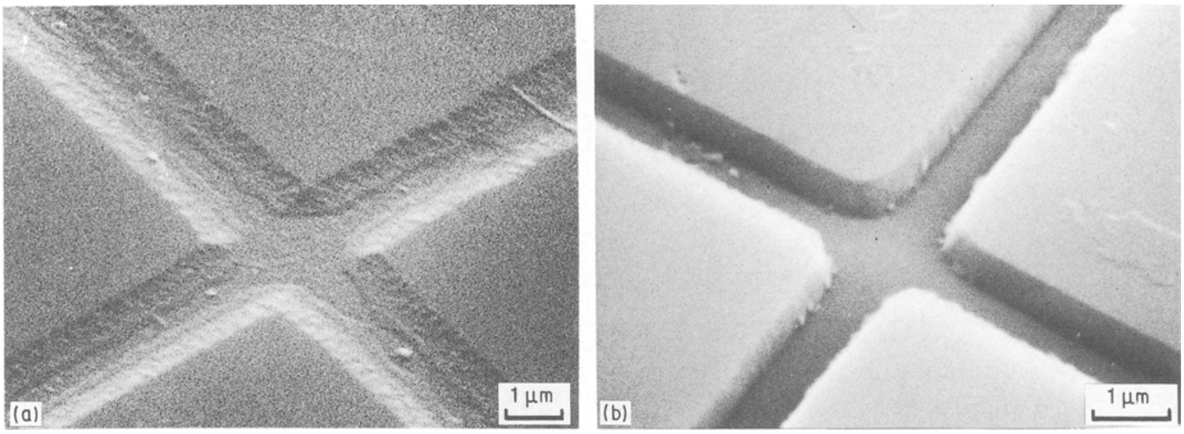

Figure 1 Comparison between SiO_2 substrates with rounded and sharp etch profiles, respectively, prior to diamond growth.

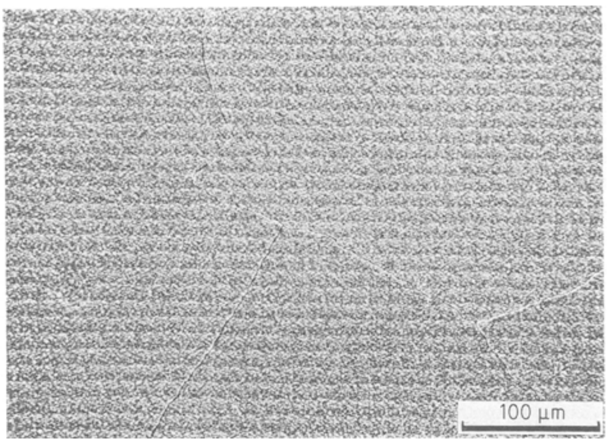

Figure 2 Surface morphology of diamond growth on patterned SiO_2. The film thickness is approximately 9 μm. Note the development of surface cracks.

of reduced material. A similar structure was observed to occur on Si substrates with sharp surface discontinuities where the plasma intensity profile is highly non-uniform.

4. Discussion

Microlithographic patterning has been applied to diamond film growth for controlled seeding [2–4] and microstructural control [2]. The current work demonstrates that, in addition to these uses, the technique offers potential improvements in film adhesion.

Even though the profiles of the initial etched lines did not have the desired undercut to physically constrain or "dovetail" the film into the substrate, the process still produced substantial improvement in film adhesion. This is believed to be partially due to increased surface area for film–substrate bonding and enhancement of fine grain nucleation and dense film microstructure. The diamond crystallites are able to grow around the sharp steps of the etched lines, following the contours of the substrate surface pattern (Fig. 5). This provides a means of resisting both planar and normal stresses which could induce film delamination. The minimal improvement in film adhesion provided by the rounded etched lines confirms that the sharp steps are critical to the effect; we anticipate that with refinement of the etching profiles, even further enhancements in film adhesion will be possible.

The cross-sectional microstructure of the diamond film immediately above the patterned regions differed significantly from the non-patterned regions, with the individual columns of the former growing at acute angles to each other and strongly impinging (Fig. 6). The cross-sectional structure far from the unetched regions was similar to that of the unetched control sample, with parallel columnar grains over the entire film thickness. The expanding, columnar structure associated with the etched lines may be instrumental

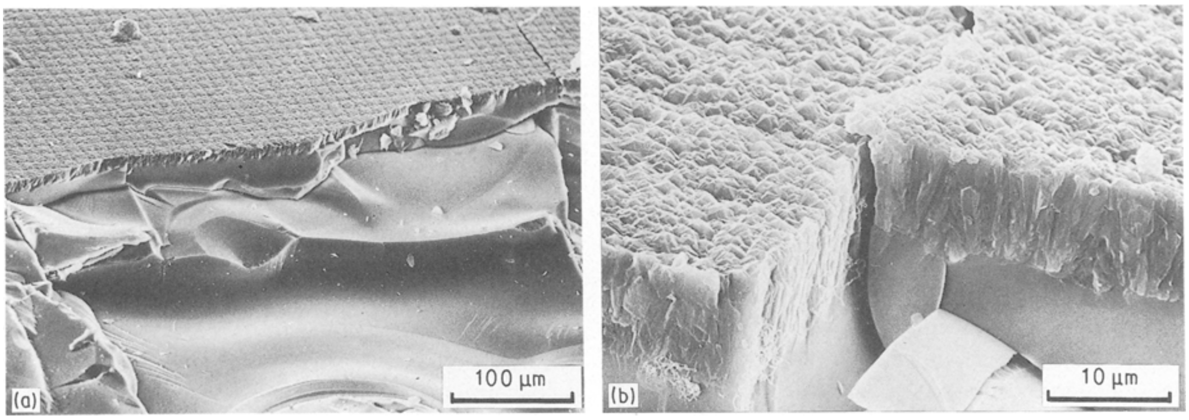

Figure 3 Cross-sectional SEM micrograph illustrating subsurface fracture in SiO_2 substrate after extended diamond growth.

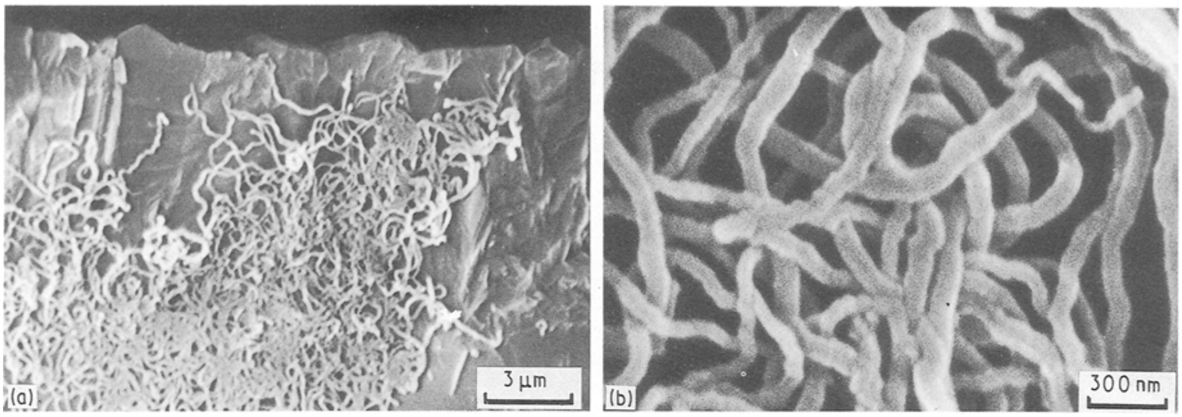

Figure 4 Filamentary microstructure observed in subsurface cracks attributed to redeposition of reduced substrate material.

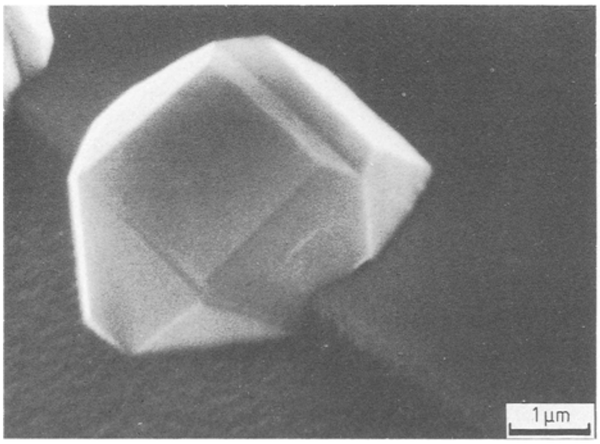

Figure 5 SEM micrograph of diamond crystallite growing around the etched feature on a Si substrate.

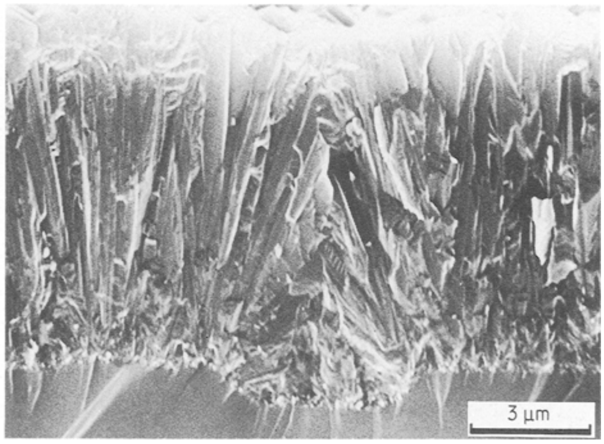

Figure 6 Cross-sectional SEM micrograph illustrating expanding columnar geometry in regions of sharply etched features in SiO_2.

in the stress characteristics of the film. An unpatterned diamond film on Si may develop significant stresses of either compressive or tensile nature during growth as evidenced by the degree of substrate curvature. The expanding columnar grain geometries in the patterned films would tend to impose compressive stresses into the films as the columns grow and impinge. These stresses may actually help to balance the net stress in otherwise tensile films. Indeed, if this is the case then by tailoring the periodic spacing of these features, one may be able to independently exercise control over the stress state of a diamond thin film. In films that would otherwise be compressive in nature, the patterning would accentuate the degree of stress. This is most likely the case in the present experiments, with the combined stresses ultimately exceeding the fracture strength of the silica substrate.

The ultimate fracture of the SiO_2 surface is likely to be due to a combination of intrinsic growth stresses and thermal expansion mismatch at the high processing temperatures. Additional reduction of the surface mechanical strength could have resulted from the hydrogen plasma environment, and further studies are required to establish this. The subsurface fracture of a substrate by a tensile thin film has been modelled by Drory and Evans [5] and Drory *et al.* [6]. The observed crack geometries in this work are identical to those described above, with both shallow and deep substrate cracks running parallel to the film interface.

Quantitative comparisons of the observed behaviour can be made to the crack depths predicted by the theoretical models and experimental validations of [5] and [6]. A substrate to film thickness ratio of 100 and an elastic modulus ratio of approximately 10 are appropriate for the current experiments. The observed ratio of crack depths to film thickness are 10 and 3.5 for the deep and shallow cracks, respectively. This compares to values of approximately 8 and 2, respectively for the predictions of [6].

5. Conclusions

Microlithographic patterning of a substrate surface prior to diamond growth provides a means of improving film adhesion beyond that of non-patterned substrates. This technique has significant application to the growth of diamond films on non-compatible substrates. The alteration of the growth geometries in the regions of the patterning may be responsible for modification of the film stress, providing a means of control over the mechanical state of the resultant diamond film. Implementation of this technique to thicker film growth for which intrinsic compressive stresses may be large, however, will require the substrate fracture stresses to be considered.

References

1. K. SPEAR, *J. Amer. Ceram. Soc.* **72** (1989) 171.
2. J. F. DENATALE, J. F. FLINTOFF and A. B. HARKER, *J. Appl. Phys.* **68** (1990) 4014.
3. JING SHENG MA, H. KAWARADA, T. YONEHARA, JUN-ICHI SUZUKI, JIN WEI, Y. YOKOTA and A. HIRAKI, *Appl. Phys. Lett.* **55** (1989) 1071.
4. A. R. KIRKPATRICK, B. W. WARD and N. P. ECONOMOU, *J. Vac. Sci. Technol.* **B7** (1989) 1947.
5. M. D. DRORY and A. G. EVANS, *J. Amer. Ceram. Soc.* **73** (1990) 634.
6. M. D. DRORY, M. D. THOULESS and A. G. EVANS, *Acta Metall.* **36** (1988) 2019.

Received 19 October 1990
and accepted 25 March 1991