DOE/ER

DOE/ER/45345--T1

DE92 010327

PROGRESS REPORT FOR THE PROGRAM

FUNDAMENTAL STUDIES OF THE CHEMICAL VAPOR DEPOSITION OF DIAMOND

for the period

April 1, 1990 to July 31, 1991

Submitted to

Metallurgy and Ceramics Branch
Division of Materials Science
Office of Basic Energy Sciences
Department of Energy
Washington, D.C. 20545

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ABSTRACT

The plasma or thermally enhanced low pressure chemical vapor deposition of diamond films is an exciting development with many challenging fundamental problems. The early stages of nucleation is relevant to the initial growth rate and the perfection and morphology of the deposit. To isolate one of the factors that influences nucleation, we have studied the effect of surface topography on the nucleation process. Our earlier work has shown preferential nucleation on sharp convex features and we have proposed several possible reasons for this behavior, including dangling bonds at the convex features. In our recent work, we have extended our investigation to include a novel patterning of silicon substrates used to pattern silicon solar cells. The results are consistent with our earlier observations that the majority of nucleation events occur on protruding surface features. In an effort to establish whether dangling bonds at the protruding surfaces may be responsible for the selective nucleation, we have evaluated the dangling bond concentration using electron spin resonance. We have carried out deposition under nominally identical surface topography, but with different concentrations of dangling bonds at or near the surface. The results of this study indicate that dangling bonds play a minor role in enhancing nucleation, in contrast to a substantial role played by special surface topographical features. In the course of the past year, we have submitted four manuscripts for publication and have made six presentations. Our pictures of diamond nucleation have been selected for two special illustrations. Also, based partially on his diamond research on the present program, Paul Dennig was selected to participate in diamond research at the National Institute for Research in Inorganic Materials (NIRIM) in Tsukuba City, Japan on a special NSF program.

1. INTRODUCTION

During the last three decades, methods for depositing diamond films by low pressure enhanced chemical vapor deposition have been developed. Early studies on this topic were devoted primarily to establishing whether true diamond was indeed deposited. Substantial progress in this field, however, has led to several reproducible deposition methods that produce high quality diamond. The critical issues currently being addressed are the deposition rate, cost, adhesion to substrates, and the morphology of the deposit. The early stages of nucleation have a major influence on these issues. Numerous studies have shown that some materials are inherently better for substrates than others. Generally, good lattice matching and carbide formers are characteristics of good substrates. Even with the best materials as substrates, however, it is common practice to enhance the nucleation by scratching the surface of the substrate with fine diamond powder. There are different opinions on why this method of nucleation enhancement is effective and the following explanations have been proposed: the polishing process modifies surface topography introducing hills and valleys which are preferred sites of nucleation; there is mechanical damage introduced which develops dangling bonds as preferred sites for nucleation; and residual diamond particles act as nucleation sites. The nature of the abraded surface is complicated and difficult to analyze. It is possible that all these mechanisms are important to varying degrees. The objective of the present study is to evaluate the importance of one of these factors, namely, the surface topography. Our approach has been to selectively etch surface features in silicon substrates using masking and chemical etching methods that are used for integrated circuit fabrication. Our previous results show that the majority of nucleation events occur on protruding surface features. In the last year, we have analyzed these results and have submitted four papers describing our results [1-4], and we append copies of three of these papers as appendix A, B, and C. In addition we have extended our study to include a new novel surface topography and have investigated whether dangling bonds on the surface may be responsible for the selective nucleation. To this end, we have employed electron spin resonance to evaluate the dangling bond concentration . We have carried out deposition under nominally identical surface topography, but with different concentrations of dangling bonds at or near the surface. The results of this study indicate that dangling bonds play a minor role in enhancing nucleation, in contrast to a substantial role played by special surface topographical features. We describe the details of this study below.

2. EXPERIMENTAL

We employ a method for modifying the substrate surface of a silicon wafer that was originally designed to minimize reflections from the surfaces of solar cells. This treatment provides an unusual surface topography with an array of convex surfaces. The surface treatment consists of masking a high-resistivity <100> oriented silicon substrate with a pseudo-random pattern of 2μm squares using standard integrated circuit photolithography techniques. The wafer is then etched in a KOH solution to form pyramids composed of (111) planes [cf. reference 5, for example]. In this surface treatment, there was no abrasion step and therefore no residual abrasive particles.

Dangling bonds can be identified by the electron spin resonance (ESR) method [6,7]. This method can be employed to detect paramagnetic species in liquids, gases, and solids. We apply the method here to evaluate silicon dangling bonds created by the surface treatment of silicon wafers. The sensitivity of this method is high and $\sim 10^{11}$ dangling bonds can be measured. In the present case, with high-resistivity float zone single crystal silicon wafers as substrates that are exposed to various surface treatments, we can evaluate the silicon dangling bonds created by surface treatments using ESR since the background of dangling bonds in the bulk silicon is very low. The available bonds on a typical silicon surface are on the order of 10^{15} cm^{-2}. For a sample surface area of $\sim 1 mm^2$, the detection limit is ~1% of the available surface bonds, with a proportionally lower detection limit for larger sample areas.

In the present study, the surface and near surface dangling bonds in the Si substrates were measured by ESR at room temperature and at a non-saturating power level. The apparatus was a Varian E-line Century Series spectrometer operating in the X band. To avoid the microwave loss arising from the induced current in the substrate, Si (100) substrates with high resistivity (~200Ωcm) were used. The samples were 1.1cm x 0.5cm with a thickness of 0.03cm, and both sides of the as-received samples had been polished to a mirror surface. Three types of samples were evaluated: a control sample which was an untreated substrate; an as-scratched sample, with one side of the sample scratched by diamond particles and then cleaned in ethanol; and an as-etched samples which was a scratched substrate that was etched in HF : HNO_3 (1:20) at room temperature to remove several microns of silicon.

The following deposition conditions were used: a deposition time of 6 hours (10 hours for the specimen shown in Fig. 5, and 1 hour for the samples studied with ESR, shown in Fig. 7); gas activation with a tantalum hot filament (~2000° C) with no applied substrate bias; a gas composition of 1% methane in a balance of hydrogen; an ambient pressure of 30 Torr; and a substrate temperature of 900-1000° C. The quality of the deposited diamond was evaluated by producing a film under identical deposition conditions. The resulting film was evaluated by SEM, Raman spectroscopy, and ESCA and was shown to be of good quality for the same deposition conditions. For the present study, the initial stages of diamond particle growth were characterized by SEM. The results are shown in Figs. 1-4. We did not attempt to compare nucleation densities quantitatively for these substrates. However, in Fig. 5, the results of deposition on a linear v-groove pattern is provided and a comparison is made between the linear nucleation density for edges of roughly 54° versus 117°.

3. RESULTS

Figure 1 shows nucleation taking place in a non uniform pattern. Such non uniformity is often observed in diamond particle nucleation, indicating that subtle surface features are important. Figure 2 is an enlargement of the region shown in Fig. 1. Nucleation takes place predominantly on the upper portions of the pyramids rather than in the crevices. Figure 3 shows nucleation occurring along a path from the lower left to upper right of the view, with Fig. 4 portraying an

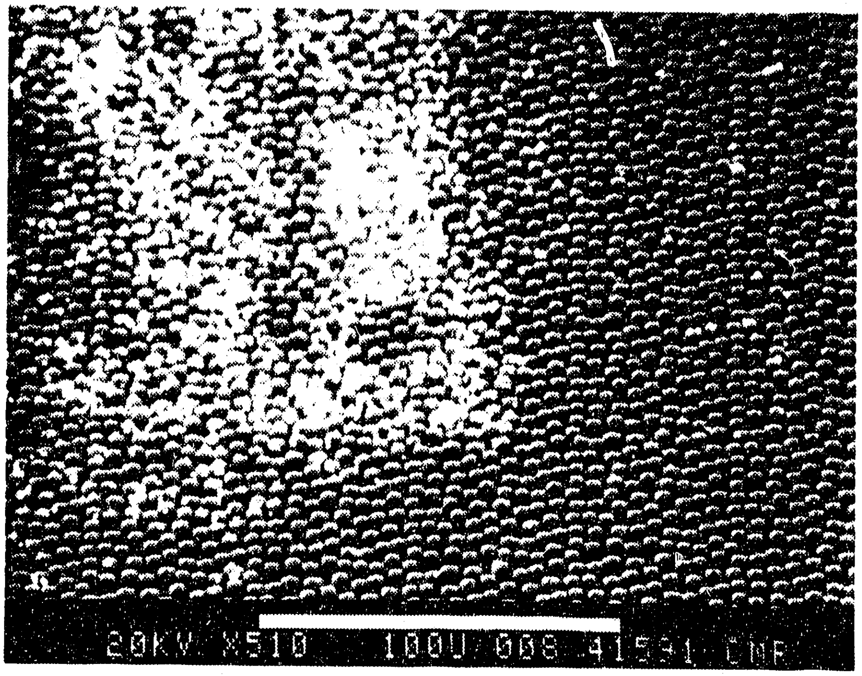

Figure 1. Enhanced nucleation on pyramids etched into <100> high resistivity silicon, 45° tilt.

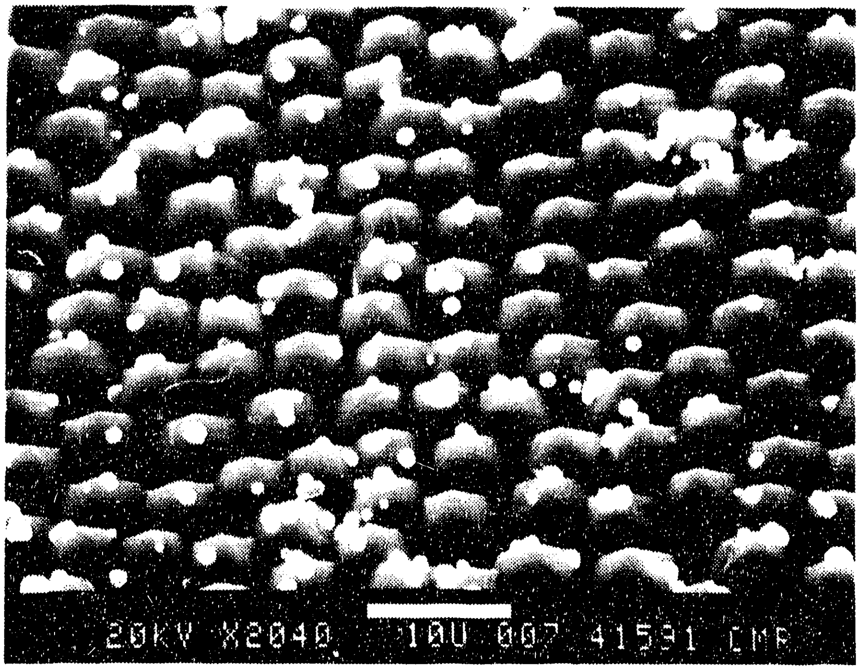

Figure 2. Enlargement of the region shown in Fig. 1, with a 45° tilt. Nucleation occurs predominantly on the upper portions of the pyramids in this location, rather than in the crevices.

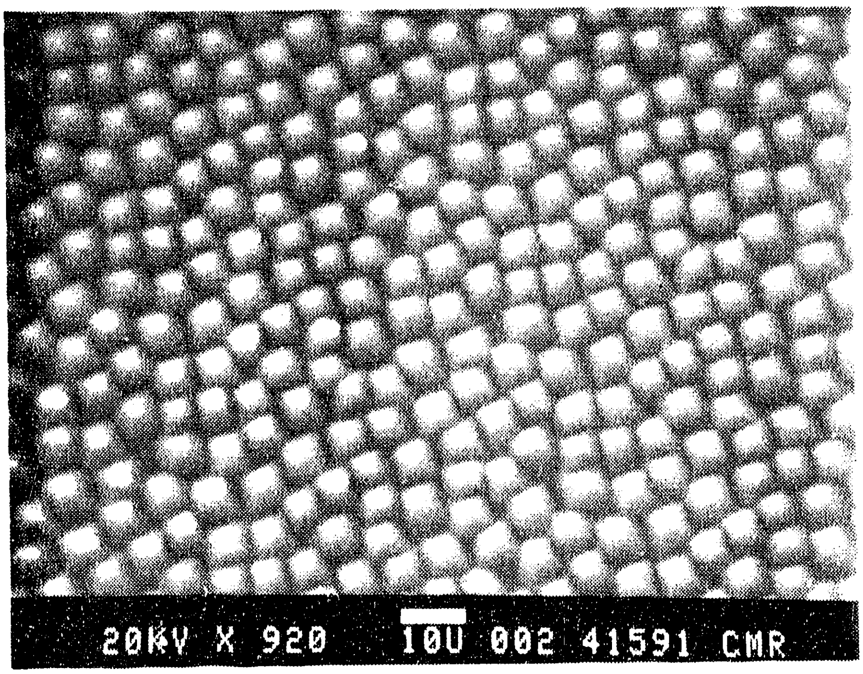

Figure 3. Nucleation on pyramids etched into <100> high resistivity silicon, 15° tilt. Nucleation occurs along a path from lower left to upper right.

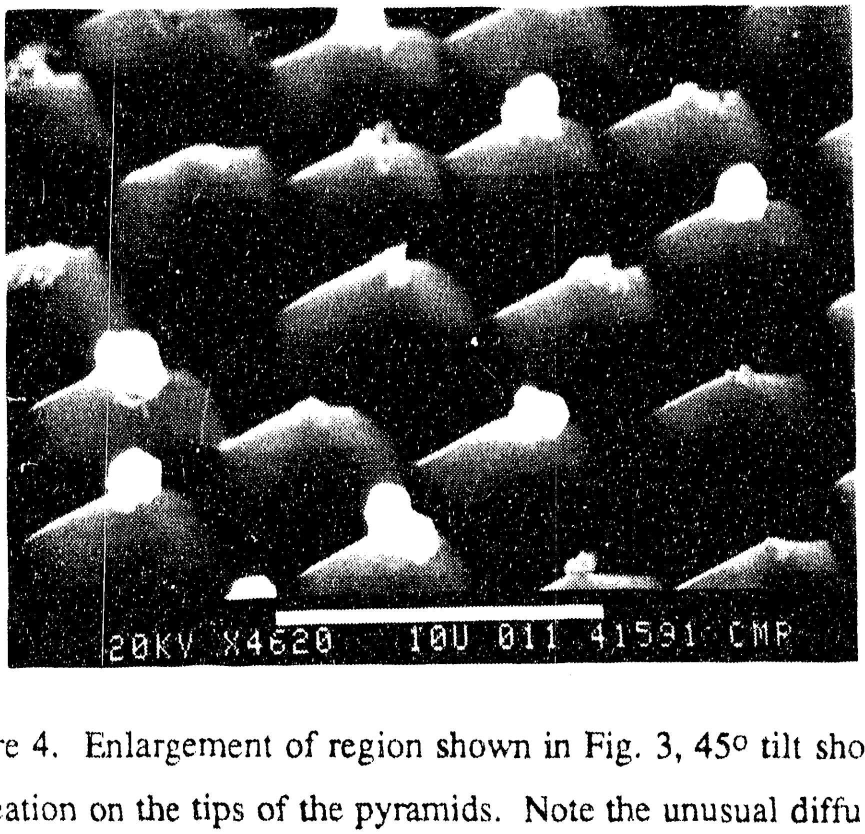

Figure 4. Enlargement of region shown in Fig. 3, 45° tilt showing nucleation on the tips of the pyramids. Note the unusual diffuse structural features on the pyramid tips in the path of nucleating particles.

enlargement of the region shown in Fig. 3. Nucleation takes place consistently on the tips of the pyramids in this location. In this experiment, we concur with the observations of Jansen, et al. [8], who report that nucleation was not observed in sharp concave features that were produced by chemical etching. In addition, we observe that nucleation takes place predominantly on convex surface features.

In Fig. 5, V-grooves of increasing width (but constant depth) are etched into a silicon <100> surface, without using an abrasion treatment. Nucleation occurs preferentially on the edges of silicon bounding the grooves. There is roughly 8 times the nucleation density (particles/unit length) on the more acutely angled edges on the left, as compared to those on the right.

Figure 6 shows the derivative of the ESR resonance peak for the three samples: a control sample which was an untreated substrate; an as-scratched sample, with one side of the sample scratched by diamond particles and then cleaned in ethanol; and an as-etched samples which was a scratched substrate that was etched in HF : HNO_3 (1:20) at room temperature to remove several microns of silicon. It is clear from this figure that scratching produces a significant concentration of paramagnetic centers. The spectrum for the scratched sample closely resembles the powder pattern for silicon dangling bonds in which the ESR signal is isotropic with respect to the orientation of the specimen relative to the DC magnetic field and has a G-value of 2.0055 [9]. The number of dangling bonds in the as-scratched sample was calculated to be 9×10^{12}. If these paramagnetic centers resided only on the surface, the density of the surface dangling bonds would be 1.8×10^{13} cm^{-2}, which is 2.6% of the available surface bonds of 6.8×10^{14} cm^{-2} on Si (100). The density of surface dangling bonds is most likely overestimated because the defects induced by scratching penetrate beneath the surface of the substrate. Furthermore, the surface dangling bonds induced by the scratching treatment are most likely passivated by oxygen because the samples were exposed to air. After etching, the ESR signal returned to a level comparable to that for the control sample. This indicates that the etching removed the mechanical damage from both the surface and the edge of the sample.

All three samples were then exposed in a hot filament reactor simultaneously for 1hr. Figure 7 shows that the nucleation density of the

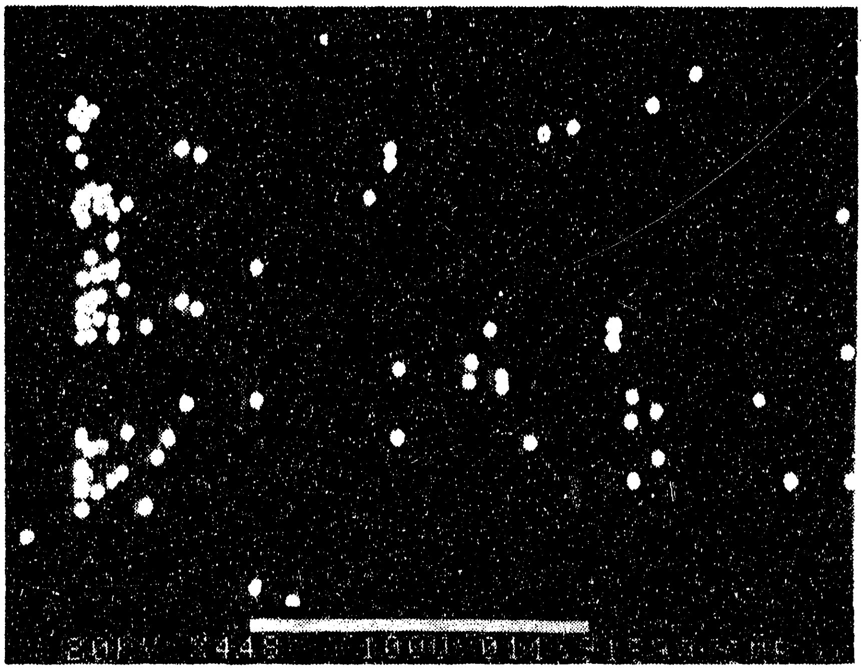

Figure 5. Enhanced nucleation on edges, 15° tilt. showing a preference for nucleation on the more acutely angled edges.

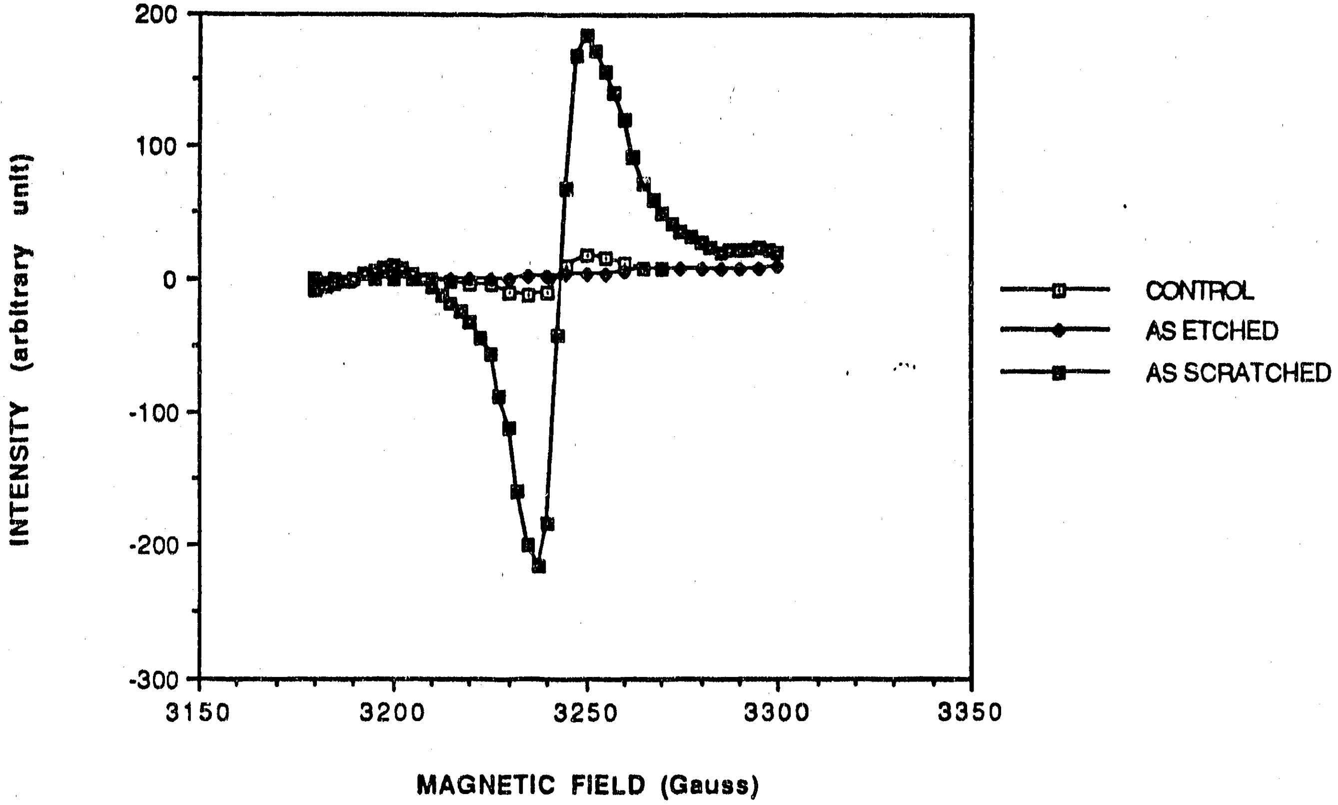

Figure 6. The derivative ESR spectrum of three samples: a control sample which was an untreated substrate; an as-scratched sample, with one side of the sample scratched by diamond particles and then cleaned in ethanol; and an as-etched samples which was a scratched substrate that was etched in HF : HNO_3 (1:20) at room temperature to remove several microns of silicon.

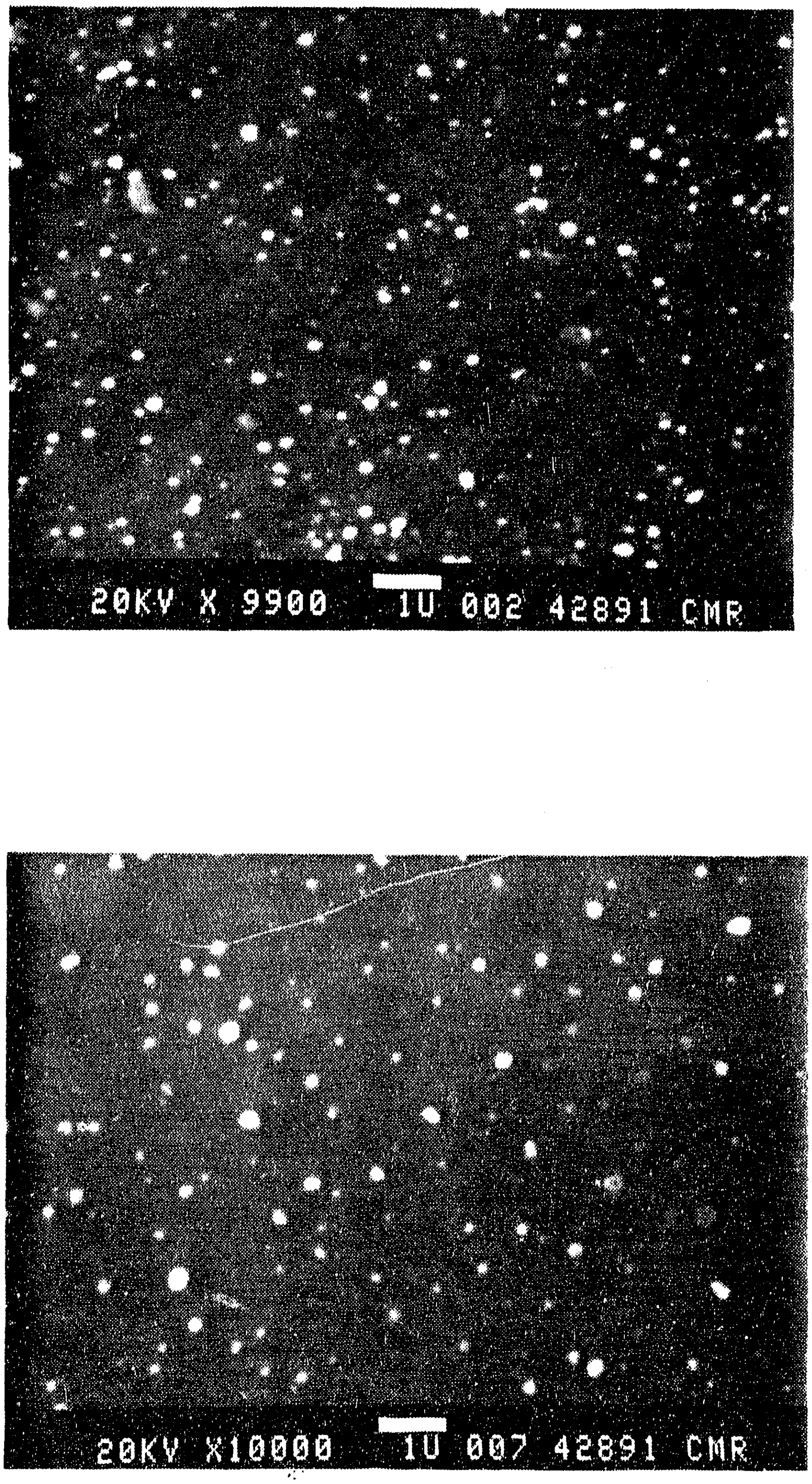

Figure 7. Nucleation on (a) as–scratched and (b) as–etched samples

etched sample (~2 x 10^8 cm^{-2}) is much nearer to that of the scratched sample (~6 x 10^8 cm^{-2}) than to that of the control sample (~0 cm^{-2}). This suggests that the substrate surface geometry plays a more significant role in nucleation than do the dangling bonds. It should be noted that the observed ESR signal that is associated with dangling bonds near the substrate surface at room temperature in air may be different from the deposition conditions and it would be more precise to measure the ESR signal under the deposition conditions.

4. CONCLUSIONS

We have previously reported our observations that nucleation of diamond from enhanced chemical vapor deposition of diamond is favored on prominent features of the substrate surface, namely, features that protrude with sharp edges or apexes, as opposed to valleys or pits [1,2]. . Our present work with pyramid textured surfaces provides additional evidence for this behavior. Among a lengthy list of possible explanations for the preferential nucleation of diamond on sharp convex edges [2], we considered the most likely to be: minimizing the interfacial energy for diamond nuclei forming on sharp convex surfaces; the presence of more dangling bonds at these sites; and a larger reactant flux at these sites. The present study compares the nucleation behavior of substrates with different dangling bond concentrations, as characterized by ESR. The results indicate that substrate surface geometry plays a more significant role in nucleation than does the dangling bond concentration.

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2. P. A. Dennig and D. A. Stevenson, Accepted for Publication in Appl. Phys. Lett.

3. P. A. Dennig and D. A. Stevenson, Accepted for publication, "Applications of Diamond Films and Related Materials"Proceedings of the First International Conference on the Applications of Diamond Films and Related Materials, August 20-22,1991, Auburn, Alabama, USA, Edited by Y. Tzeng et al

4. P. A. Dennig, H. Shiomi, N. M. Johnson, and D. A. Stevenson, Submitted for publication, Thin Solid Films

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6. PUBLICATIONS AND PRESENTATIONS

P. A. Dennig and D. A. Stevenson, 2nd International Conference on the New Diamond Science and Technology, Washington, D. C. Sept. 23-27, 1990, Special Series Volume, code NDST-2, "Influence of Substrate Topography on the Nucleation of Diamond Thin Films"Materials Research Society (MRS), R. Messier and J.T. Glass, eds. July; 1991. pp. 403-408

P. A. Dennig and D. A. Stevenson, Accepted for Publication in Appl Phys. Lett.

P. A. Dennig and D. A. Stevenson, Accepted for publication, "Applications of Diamond Films and Related Materials"Proceedings of the First International Conference on the Applications of Diamond Films and Related Materials, August 20-22,1991, Auburn, Alabama, USA, Edited by Y. Tzeng et al

P. A. Dennig and D. A. Stevenson, Submitted for publication, Thin Solid Films

Presentations:

Oral Presentation: Bay Area High Temperature Science Symnposium, Lawrence Berkeley Laboratories, November 28, 1990

Poster Presentation: National Science Foundation Site Visit, Stanford University, October 29, 1990

Poster Presentation: 2nd International Conference on the New Diamond Science and Technology, Washington, D. C. Sept. 23-27, 1990,

Oral Presentation: Industrial Affillilates Annual Meeting, Department of Materials Science and Engineering, Stanford University, January 31, 1991

Poster Presentation: Diamond Films Science and Technology Workshop, Stanford Linear Accelerator Center, February 1, 1990

Poster Presentation: First International Conference on the Applications of Diamond Films and Related Materials, August 20-22,1991, Auburn, Alabama

Special recognition:

Micrographs of our diamond deposition were selected for illustrations for two separate publications

Based on his academic record and his research in diamond deposition on the present DOE program, Paul Dennig was selected for participation in the special NSF Summer Program for US scholars to do research in Japan. He is participating in Diamond Research at the National Institute for Research in Inorganic Materials (NIRIM) in Tsukuba, Japan

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