

The effect of nitrogen on competitive growth mechanisms of diamond thin films

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Abstract

The correlation between surface morphology and texture (distribution of crystal orientations) has been analyzed to determine how nitrogen provides a competitive growth advantage for the formation of $\langle 001 \rangle$ texture in diamond films. The film morphologies were measured using TappingMode[®] atomic force microscopy. Corresponding texture studies were performed using X-ray diffraction with a four-circle goniometer to measure (111), (220) and (400) pole figures. Orientation distributions were generated from the pole figures, from which inverse pole figures were made to quantify how texture was affected by process variables. After 2 h of growth, with and without nitrogen, similar textures were observed. With increasing time, nitrogen stimulates the growth of orientations between $\langle 001 \rangle$, $\langle 114 \rangle$, and $\langle 104 \rangle$. Without nitrogen, the majority orientation is $\langle 101 \rangle$ with a secondary component near $\langle 113 \rangle$. Examination of fracture surfaces indicates correlations with the observed texture and morphology changes. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Diamond thin films are emerging as strategic materials for a variety of diverse applications such as piezoresistive sensors [1], windows and MEMS (micro-electro-mechanical systems). The size of the crystallites and the texture of the film play important roles in the intended function [2–6]. Nitrogen in particular has been shown to affect both morphology and texture [7–13]. The motivation for this work was to understand the effects of nitrogen on the competitive evolution and growth of $\langle 001 \rangle$ versus $\langle 101 \rangle$ fiber texture.

2. Reactor design and deposition conditions

A 2.45 GHz microwave plasma cavity reactor with a 12.5 cm maximum discharge was used to deposit poly-

crystalline diamond films on 7.62 cm diamond scratch-seeded (100) p-type silicon wafers. Each sample in this study was grown at a reactor pressure of 38.4 Torr with flow rates between 202 and 217 sccm. The substrate temperature was controlled mainly by the operating pressure [14]. Calibration experiments showed that with an operating pressure of 38.4 Torr, the substrate temperature was approximately 825°C. The deposition system was combined with a computer controlled ultrahigh vacuum gas handling system which allowed careful control of the gas input variables. Typical leak rates were approximately 0.25 mTorr/h. Input gases of research and ultrahigh purity were used: 99.9995% hydrogen, 99.99% methane and 99.9995% hydrogen/nitrogen mix. The nitrogen was introduced via a pre-mixed gas of 2% nitrogen in hydrogen. Gas phase nitrogen concentrations were monitored by calibrated optical emission spectroscopy (OES), using the cyano (CN) band transitions between 385 and 390 nm, similar to the method described in Ref. [12]. In calibration tests, an increase of 10 ppm nitrogen in the gas phase

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was detectable in the OES emission spectrum. Based on our calibration experiments, we give an estimate of 10 ppm nitrogen concentration as our ‘0 ppm’ nitrogen concentration. Further deposition details may be found in Ref. [8].

The total weight gain for each sample was measured using a Denver Instruments Analytical Balance model M-220D, accurate to 0.01 mg. The total weight gain was used to calculate an approximate growth rate. No significant differences in growth rates with or without nitrogen were observed in these depositions under these reactor conditions.

3. Analytical strategy

All the samples described in this study were 1 cm² pieces cut from the center of each deposition. The depositions were relatively uniform over this center area, although radial variations and rings were noted further out [15]. The studies of columnar growth were performed on a Leicascan 360 FE scanning electron microscope.

Atomic force microscope (AFM) imaging and analyses were performed using a Digital Instruments[®] Nanoscope IIIa operated in ambient air. TappingMode[®] AFM was employed, using TappingMode[®] etched silicon probes with a nominal

tip radius of curvature of 5–10 nm, and a 13 × 13 μm ‘E’ scanner.

The (111), (220) and (400) pole figures were measured on each specimen using 5° angular increments up to a tilt angle of 80°, and using counting times which were longer with smaller film thicknesses. Following procedures outlined in Ref. [16], the raw data was corrected for defocusing and normalized using an analytical procedure. The lack of experimental defocusing data implies that small, but systematic, errors are present in the data, but comparisons are meaningful. Although the diamond peaks do not overlap silicon peaks, channeling effects from silicon background radiation may also be present in the measurements, since the diamond thin films are thin compared to the penetration depth of the X-rays. A harmonic analysis was done to complete the rim of the pole figures, assuming only mirror symmetry about the normal axis. The crystal orientation distribution was determined with the same symmetry assumptions in the form of a sample orientation distribution using the WIMV (Williams, Imhoff, Matthies, Vinel) algorithm, and iterating until the error between the distribution and the experimental measurements was less than 15%. From the orientation distribution, inverse pole figures were extracted from the sample orientation distribution by projecting it along the specimen normal direction. The inverse pole figures show the probability that a particular crystallographic vector points in the normal direction.

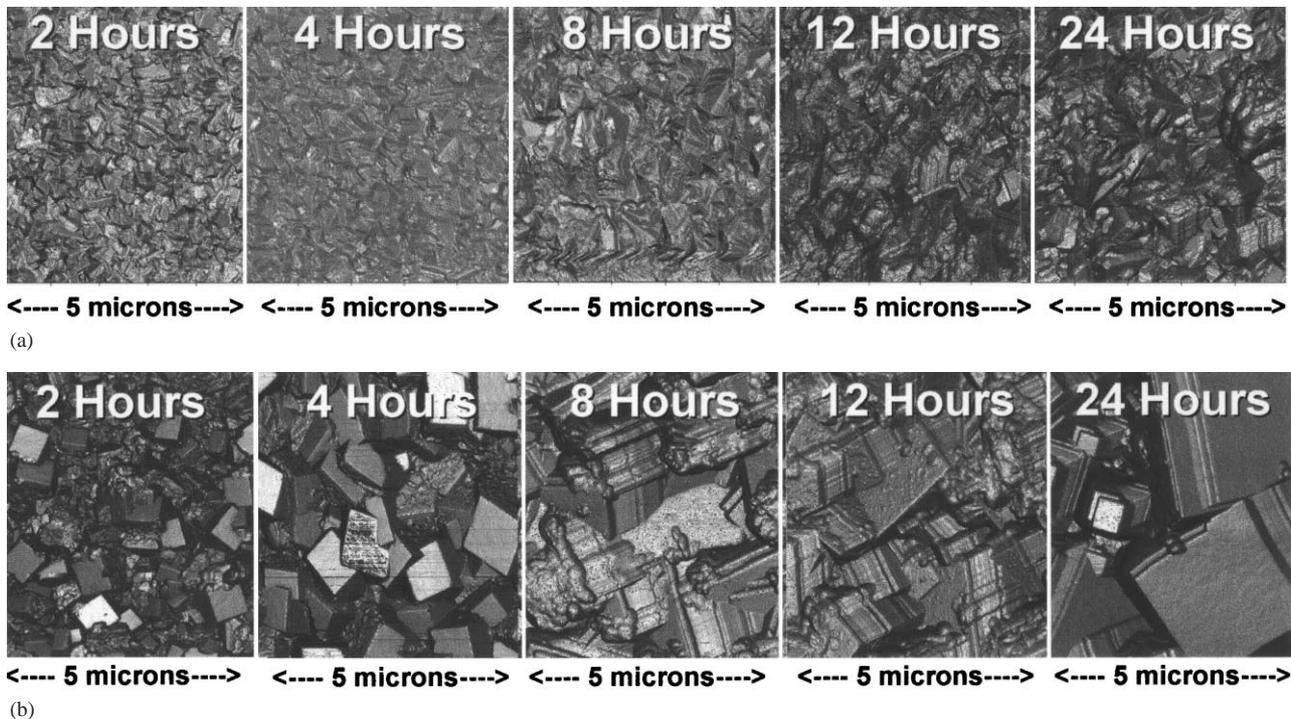


Fig. 1. Surface morphology shows coarsening as a function of time for diamond films grown with 1% methane/hydrogen at: (a) $p = 39.4$ Torr, $T = 825^\circ\text{C}$ and 0 ppm nitrogen; (b) $p = 38.4$ Torr, $T = 825^\circ\text{C}$ and 200 ppm nitrogen. The effect of nitrogen in stimulating (100) facets is apparent after 2 h of growth.

4. Experiments

4.1. Evolution of morphology and texture versus 0–1000 ppm nitrogen

Diamond films were grown for 8 h using 1% or 2% methane/hydrogen ratios, and nitrogen levels between 0 and 1000 ppm. The 8 h deposition time corresponded to the onset of a defined texture. Variations in surface morphology and film texture as a function of increasing nitrogen levels were measured. As reported in Ref. [17], multiple abrupt transitions in surface morphology were observed as nitrogen concentrations were varied from 0 to 1000 ppm. With increasing nitrogen, the morphologies observed were: fine grained (2% methane/hydrogen) or micron sized (1% methane/hydrogen) crystallites; small crystals with larger islands; larger crystals with square faces on the surface; and larger crystals with ledges and curved edges at the highest nitrogen concentrations. The transition to a (100) facet surface morphology occurred at lower concentrations of nitrogen for the 1% methane/hydrogen films than for the 2% methane/hydrogen films. This observation differs from that reported in Ref. [12] which suggests that particular reactor conditions (our pressure and temperature were not independent) and geometry may influence the effect of nitrogen.

Inverse pole figures with increasing nitrogen concentration were reported in Ref. [17]. A single transition in fiber texture from $\langle 101 \rangle$ to near $\langle 001 \rangle$ was observed for both 1% and 2% methane/hydrogen samples as a function of increasing nitrogen. For both the 1% and 2% series, a $\langle 102 \rangle$ texture rather than a $\langle 001 \rangle$ texture corresponded with the initial appearance of the (100) faceted surface morphology. This was probably due to the surface versus volumetric nature of the AFM and X-ray diffraction measurements. With higher nitrogen concentrations, the dominant texture components were within an orientation spread between $\langle 104 \rangle$, $\langle 114 \rangle$ and $\langle 001 \rangle$ for both the 1% and 2% methane/hydrogen samples.

4.2. Evolution of morphology and texture versus time, with 0 and with 200 ppm nitrogen

To investigate how a growth advantage for $\langle 101 \rangle$ (no nitrogen) or near $\langle 001 \rangle$ (with nitrogen) orientations develop with increasing thickness, morphology and texture measurements were made on specimens with growth times between 2 and 24 h. The 1% methane/hydrogen depositions grown with either 0 or 200 ppm nitrogen were studied as these allowed a comparison of $\langle 101 \rangle$ and $\langle 001 \rangle$ surface morphology/texture.

The evolution of the surface morphologies with

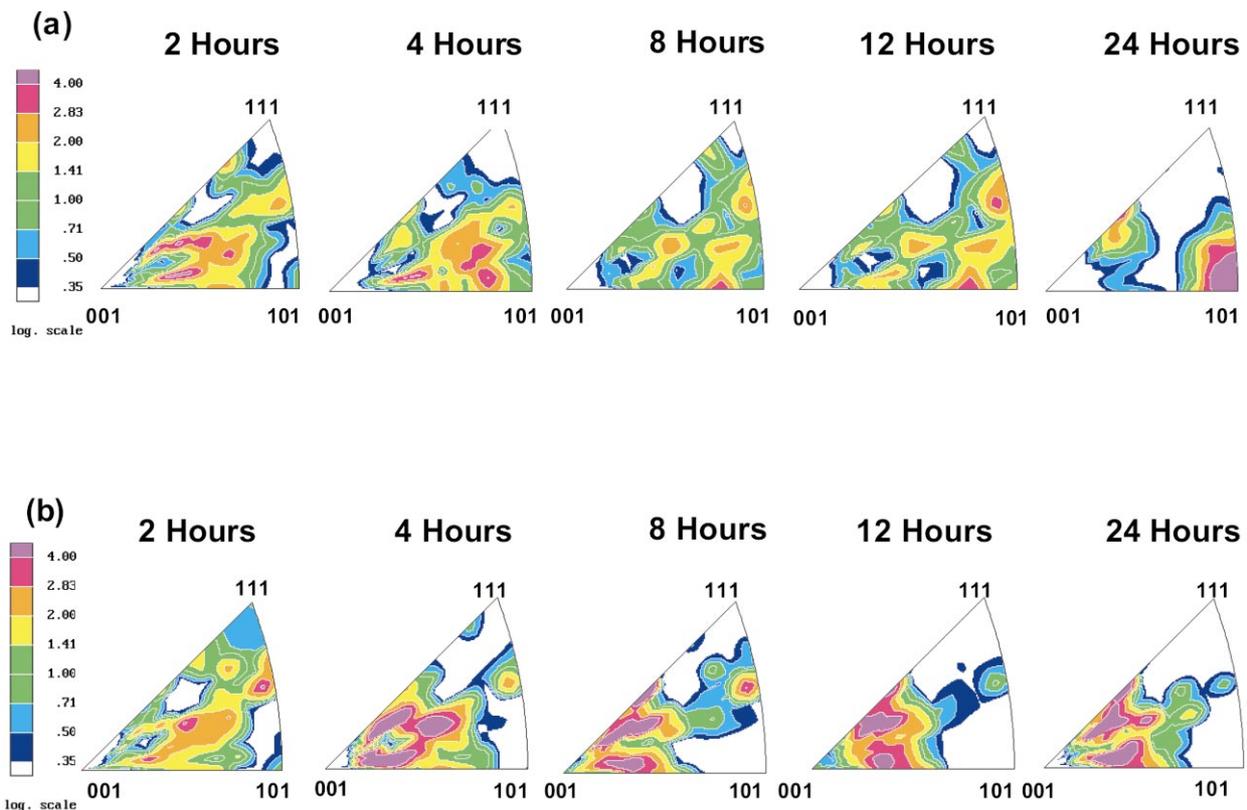


Fig. 2. Inverse pole figures show: (a) development of $\langle 101 \rangle$ fiber texture with increasing time; (b) development of an orientation spread between $\langle 001 \rangle$, $\langle 104 \rangle$ and $\langle 114 \rangle$ with increasing time.

increasing deposition time are shown in Fig. 1a for 0 ppm nitrogen, and in Fig. 1b for 200 ppm nitrogen. After 2 h of growth, the surface morphologies were already distinct with the 0 ppm nitrogen sample showing crystallographic facets that resemble rooftops (which are from $\langle 101 \rangle$ normals close to the sample normal direction) and the 200 ppm nitrogen sample showing square (100) facets. The surface crystallite sizes were generally bigger with increasing deposition time, but for the 8 and the 12 h depositions, ledges or faults were observed with and without nitrogen. The images shown in Fig. 1 are TappingMode[®] AFM images with the light source projected directly overhead. Therefore, the brightest square facets have a (100) normal close to the sample normal direction.

The corresponding evolution of the texture with increasing deposition time is shown in Fig. 2a for 0 ppm nitrogen, and in Fig. 2b for 200 ppm nitrogen. All of the inverse pole figures are plotted with the highest contour at four times random — e.g. for the 0 ppm nitrogen/24 h growth inverse pole figure, the highest value indicates that there is a probability of greater than four times that of a random sample for a crystal having a $\langle 101 \rangle$ vector pointing in the specimen normal direction (a random sample has the same probability for any crystal direction pointing in the normal direction).

After 2 h of growth there are about four major orientations which also persist through 4 h of growth. However, after 4 h there is strengthening of components near $\langle 114 \rangle$ with nitrogen, and weakening of the same orientation without nitrogen. Also in the sample without nitrogen, a component near $\langle 203 \rangle$ appears which is not present in the specimen with nitrogen. With increasing time, further growth selection is evident such that $\langle 101 \rangle$ orientations dominate without nitrogen, and orientations between $\langle 104 \rangle$ and $\langle 114 \rangle$ dominate with nitrogen. With nitrogen, there is a slight but consistent preference for orientations near $\langle 114 \rangle$. Without nitrogen, there is a secondary component near $\langle 113 \rangle$. Our observations show that the presence of nitrogen favors the growth of orientations near, but not typically at, $\langle 001 \rangle$.

Scanning electron micrographs (SEM) of the 24 h film thicknesses with 0 and 200 ppm nitrogen are shown in Fig. 3a and b respectively. Both images show that columnar growth occurs, similar to the observations of Wild et al. [10]. The largest cleavage face is comparable to the largest surface crystal topological feature. A band of less than 1 μm of extremely fine crystallite sizes is observed in both micrographs at the substrate interface (see higher magnification insert areas in Fig. 3). Above a thickness of 3 μm , large crystallites are dominant. It is apparent in these micrographs that the preferred

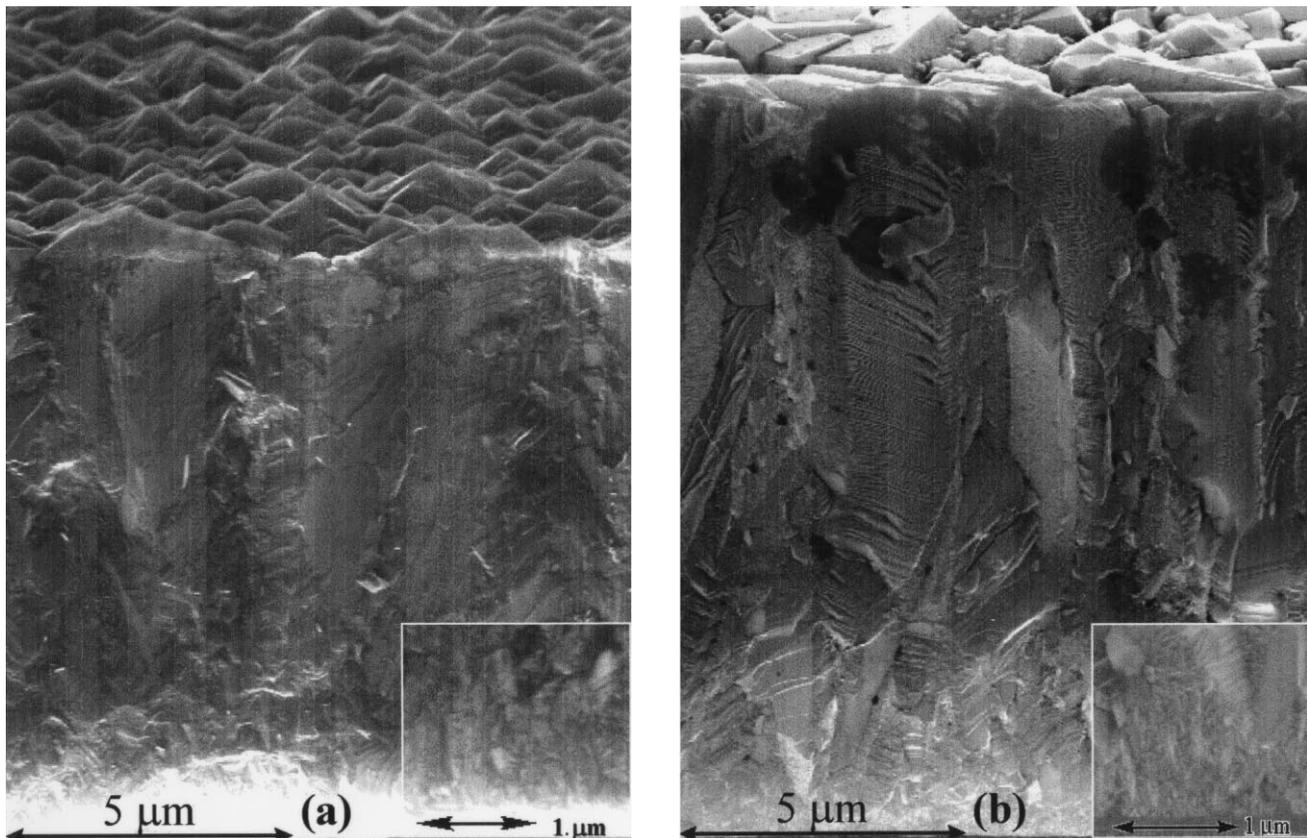


Fig. 3a. SEM micrographs of fracture surfaces show fine grained initial followed columnar growth of preferred orientations: (a) with 0 ppm nitrogen; and (b) with 200 ppm nitrogen.

growth orientation is established after about 1 μm of fine grained microstructure growth. This early layer of fine grained microstructure correlates with the 2 h texture observations, in which a similar group of dominant components has developed both with and without nitrogen. The development of the final dominant components commences after 2 h and is well developed at 24 h.

5. Conclusions

Our experiments indicate the following for diamond film depositions performed in our reactor system. Nitrogen has an important role in stimulating growth of orientations between $\langle 001 \rangle$, $\langle 114 \rangle$ and $\langle 104 \rangle$. With nitrogen there is a slight, but consistent, preference for orientations near $\langle 114 \rangle$. Without nitrogen the majority orientation is $\langle 101 \rangle$ but we also observe a secondary component near $\langle 113 \rangle$. The development of the $\langle 114 \rangle$ and $\langle 113 \rangle$ components is currently under investigation.

The evolution of the surface morphologies as a function of time indicated that after 2 h of growth:

- the surface morphologies were already distinct, with the 0 ppm nitrogen sample showing (110) facets and the 200 ppm nitrogen sample showing square (100) facets;
- the crystallite sizes were approximately 0.3 μm for 0 ppm nitrogen and 0.5 μm for 200 ppm nitrogen — neither topology was uniformly fine-grained so we expect that 2 h is above the first layer of growth; and
- no major difference in surface topography other than coarsening was observed between 2 and 24 h, although ledges were evident at 8 and 12 h both with and without nitrogen.

In the SEMs of the 24 h film thicknesses with both 0 and 200 ppm nitrogen, we observed a band of less than 1 μm of extremely fine crystallite sizes, an intermediate band of mixed small and large crystallites, and mostly large crystallites above a thickness of 5 μm . Coupling

these observations with the texture analysis indicates that the preferred growth orientation is established after about 1 μm of fine grained microstructure growth. This early layer of fine grained microstructure correlates with the 2 h texture observations in which a similar group of dominant components developed both with and without nitrogen.

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