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Growth kinetics of (100), (110), and (111) homoepitaxial diamond films

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Growth kinetics of (100), (110), and (111) homoepitaxial diamond films

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Abstract

We present the first investigation of the growth kinetics of diamond films grown homoepitaxially by hot-filament chemical vapor deposition on (100), (110), and (111) natural diamond substrates. Growth rates on the various faces exhibited different functional dependences on CH_4 flow rate, being linear on (100), slightly sublinear on (110), and sigmoidal on (111). The temperature dependence of the growth rate was also crystal-face-dependent, yielding effective activation energies of 7.6 ± 3, 17.8 ± 2, and 11.6 ± 4 kcal/mol for <100>, <110>, and <111> growth, respectively, at substrate temperatures between 735 and 970 °C. The apparent activation energies were considerably larger at substrate temperatures between 675 and 735 °C. Implications of the observed kinetics for diamond growth mechanisms are discussed.

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Diamond film growth by chemical vapor deposition (CVD) has burgeoned rapidly during the past decade, accompanied by considerable progress in fundamental understanding.[1] Particular progress has been made in understanding chemistry taking place in the gas phase above the substrate[1,2] and in identification of the precuror(s) primarily responsible for growth,[3,4] but the details of reactions taking place on the growing surface are as yet unknown. However, despite the commercial importance of high growth rates and the potential for gaining insight into the details of the growth mechanism, only a handful of studies of the growth kinetics of polycrystalline diamond films have been reported.[5-9]

There is a clear but unmet need for systematic studies of CVD growth kinetics on individual crystal faces of diamond. Interpretation of the growth kinetics of polycrystalline films is complicated greatly by the presence of both (100) and (111) crystal faces under typical growth conditions, whose relative areas depend on both the substrate temperature and the composition of the gas phase.[1] All detailed diamond growth models proposed to date have focused on a particular crystal face, including flat or stepped (100),[10-12] (110),[13,14] and (111)[15-18] orientations. Comparisons between model predictions and experimental growth kinetics of polycrystalline films implicitly assume that the surface "growth site" and the detailed growth mechanism are the same on each crystal face. Existing evidence suggests that neither assumption is valid. Recent scanning tunneling[19] and atomic force microscopy[20] studies have identified clear differences in the nanometer-scale morphologies of CVD-grown (100), (110), and (111) diamond homoepilayers, and Spitsyn and co-workers[21] found differences in the dependence of growth rate on substrate temperature between the (100) and (111) facets of diamond microcrystals. The Russian work was not well-documented, however, and involved transport of carbon gasified from graphite rather than conventional CVD.

We have grown homoepitaxial diamond films by hot-filament CVD in a reactor that has been described in detail previously.[3(a)] Most of the results presented below were obtained by injecting both H_2 and CH_4 above five 0.13-mm-diameter, 10-mm-long tungsten filaments held at 2160 °C, as measured by optical pyrometry, and located 10 mm above the substrates. Additional results were obtained by injecting the CH_4 between the filament and sample.[3(a),3(b)] (100), (110), and (111) type 2A natural diamond substrates,[22] $1.5 \times 1.5 \times 0.1$ mm^3 in dimension, were mounted side-by-side on a 0.06-mm-thick platinum ribbon which functioned simultaneously as a substrate holder and heater.[3(b)] Sample temperatures were monitored by a Pt/Pt13%Rh thermocouple spot-welded directly to the platinum ribbon. Flow rates of CH_4 were varied between 0.1 and 3 sccm, and the H_2 flow rate and reactor pressure were held at 150 sccm and 25 Torr, respectively, in each growth experiment. The films were characterized by Raman spectroscopy and by optical microscopy. The (100) and (110) films were graphite-free but the (111) films showed some graphitic inclusions and cracked due to tensile stress for film thicknesses greater than 3-4 μm.[3(b)] The growth rate measurements were performed by growing films at a given CH_4 flow rate and substrate temperature

for 1 hour, removing the substrates from the reactor, and measuring the change in thickness (≈ 0.1 μm accuracy) from the interference fringes in transmission Fourier-transform infrared spectra.[3(b)]

The dependence of growth rate on CH_4 mole fraction on each of the three substrate orientations is shown in Fig. 1. We found that the filaments became poisoned for CH_4 concentrations greater than 0.8% injected above the filament, as evidenced by reduced growth rates even after reducing the CH_4 flow rate. Reproducibility of the growth rates from sample to sample is illustrated by the scatter in the points at 0.4% CH_4. Growth rates were highest on (110) substrates; the (111) rate exceeded the (100) rate below 0.45% and above 0.7% CH_4 but was less than the (100) rate between 0.45% and 0.7% CH_4. This behavior is consistent both with previous homoepitaxial growth rate observations[3(b),5(b),5(c),23-26] and with the growth of cubooctahedral microcrystals with (100)/(111) surface-area ratios that depend on growth conditions.[1] A more interesting observation is that the functional dependence of the growth rate on CH_4 mole fraction is *different* on the three substrate orientations, being linear on (100), slightly sublinear on (110), and sigmoidal on (111).

The results from experiments where CH_4 was injected between the filament and sample (Fig. 1, open symbols) were very similar to the case where CH_4 was injected above the filament (Fig. 1, filled symbols). The main difference in the former case is a higher effective CH_4 concentration since the point of injection was closer to the substrate. Multiplication of the CH_4 mole fractions by the empirical factor 1.4 is able to essentially account for the higher effective concentration, as the scaled data are essentially superimposable on the data corresponding to injection above the filaments (Fig. 1). However, on (110) the growth rate declined for (actual) CH_4 mole fractions above 0.5% injected below the filament, which contrasts with the smoothly increasing behavior for CH_4 injected above the filament. Another difference is that the filament apparently did not become poisoned as readily when CH_4 was injected below the filament, probably due to a lower hydrocarbon concentration at the filament, and the linearity in growth rate of (100) films with CH_4 percentage extended up to 1.6%, yielding a growth rate of 6 μm/hr.

Analysis of gases collected near the substrate via sampling tubes, as described previously,[3(a)] revealed a linear dependence of methane concentration on the mole fraction of CH_4 injected. The acetylene concentration was intermediate between first and second-order in the CH_4 mole fraction, consistent with $C_1H_n \rightleftharpoons C_2H_m$ interconversion on or near the hot filament. The coincidence between the superlinear rise in growth rate on the (111) substrate and in relative acetylene concentration suggests that C_2H_2 may contribute to [111] growth at higher CH_4 mole fractions, although at 0.34% CH_4 the dominant precursor is CH_3.[3] The growth chemistry is complex, however, and other interpretations are possible.

The dependence of the growth rate on substrate temperature at a CH_4 mole fraction of 0.4% is summarized in Fig. 2 in the form of an Arrhenius plot. The growth rates on (100), (110), and (111) substrates each increase significantly with substrate temperature. The effective activation energies (slopes) appear to change near 1000 K (727 °C), although the data are unable to distinguish between

a sharp break and a gradual change in slope. Qualitatively similar growth-rate dependences, including a maximum in the range of 900-1050 °C, have been observed previously.[5,6,8] Perhaps the most important result from Fig. 2 is that the effective activation energies are *different* on the three crystal faces. Linear least-squares fits to the data over the temperature range of 735–970 °C yielded effective activation energies of 7.6 ± 3, 17.8 ± 2, and 11.6 ± 4 kcal/mol for <100>, <110>, and <111> growth, respectively, where the uncertainty estimates are calculated at the 95% confidence level. The statistics are much worse for growth at the lower temperature range of 675–735 °C and we are not able to determine whether the activation energies on the different substrate orientations are significantly different. A fit to the combined data yields an effective activation energy of 47±19 kcal/mol, which is much larger than the values at higher temperature. This activation energy is too large to correspond to a single rate-limiting step involving hydrogen abstraction, but likely includes contributions from decreases in the rates of gas-phase reactions and possibly from surface "poisoning" (e.g., by sp^2-bonded species[16(d)]) in addition to the gas-surface reaction kinetics.

Interpretation of the kinetics is complex, unfortunately. AFM studies have shown that diamond homoepilayers generally do not have ideal structures–(100) films may have variable step densities and/or pyramidal features and penetration twins; (110) films may be smooth at the nanometer scale yet exhibit local slopes deviating by 40° and more from the [110] direction; and 10-50 nm roughness on the ≈ 100 nm scale has been observed on (111) films.[20] We also observed growth-condition-dependent (100) morphologies in the present study, and believe that differences in the surface morphology (step/defect density, etc.) from sample to sample were responsible for much of the scatter in the growth-rate data. The AFM work provided evidence that diamond growth takes place primarily at atomic steps;[20] the present results imply that the growth sites (i.e., type of atomic step) and detailed growth chemistry are *different* on (100), (110), and (111) crystal planes.

In summary, the dependence of the growth rate of (100), (110), and (111) homoepitaxial diamond films on hydrocarbon concentration and substrate temperature in hot-filament CVD has been determined for the first time. Significant differences are found between the behavior on the crystal faces, implying that the details of the growth chemistry are different. Net activation energies in range of 8-18 kcal/mol for substrate temperatures between 735 and 970 °C were obtained. Further experimental and modeling work is needed in order to better understand the relationship between the observed activation energies and the kinetics of elementary gas-surface reactions and to quantify the dependence of growth rate on surface morphology.

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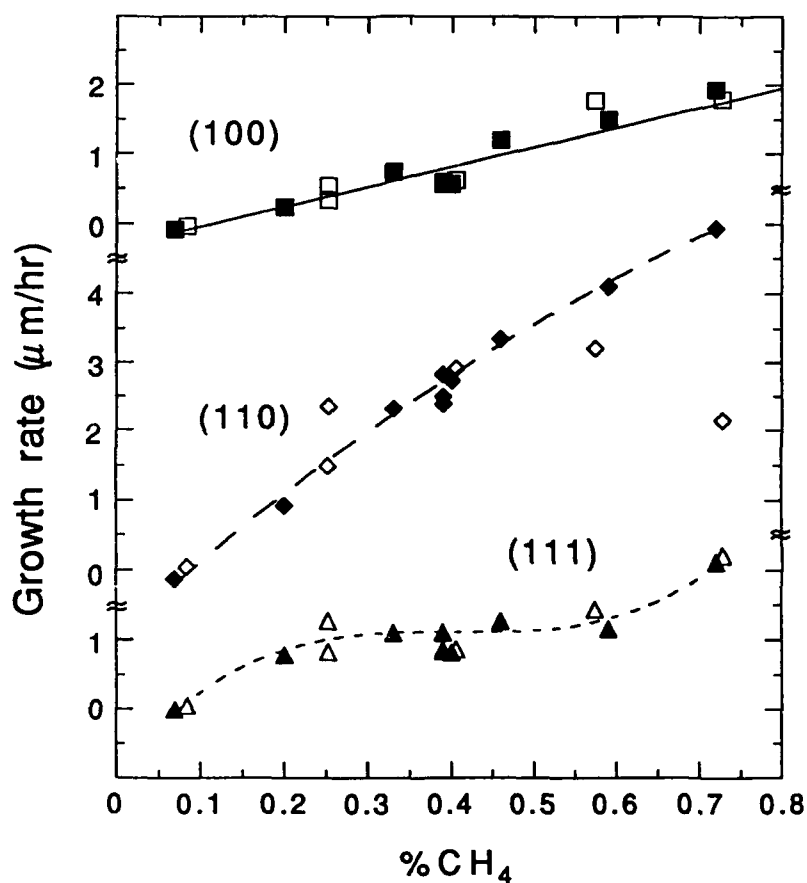
FIG. 1. Dependence of homoepitaxial growth rate on methane mole fraction at a substrate temperature of 970 °C for growth on (100) (squares), (110) (diamonds), and (111) (triangles) orientations. CH_4 was injected above (filled symbols) or below (open symbols) the filaments. The CH_4 concentrations for below-filament injection have been multiplied by 1.4 (see text).
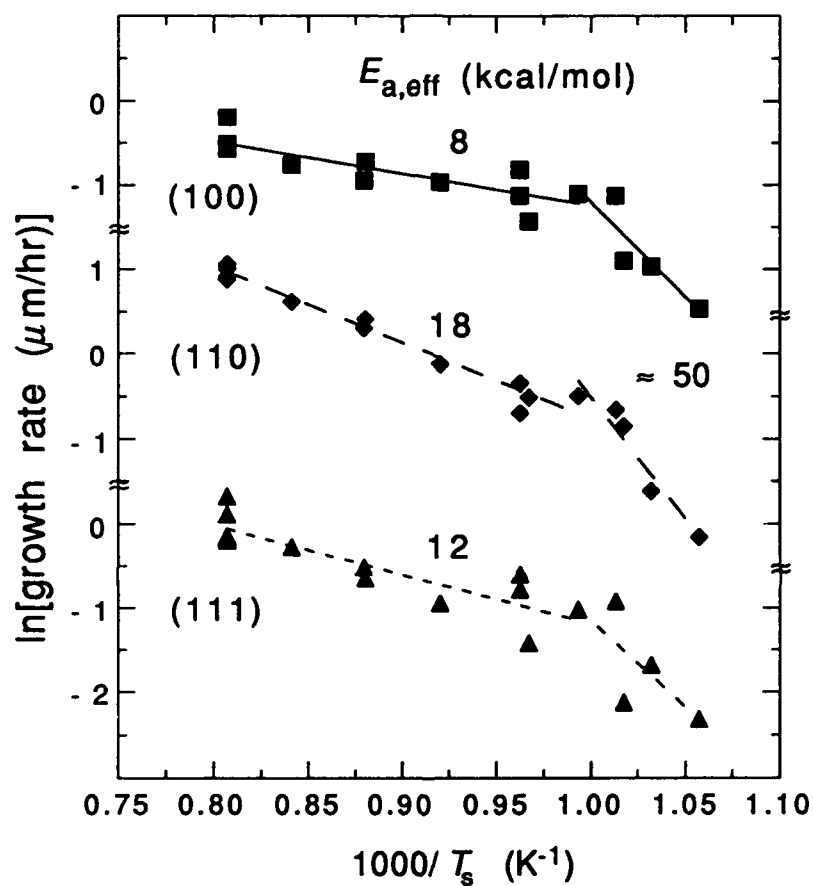
FIG. 2. Dependence of homoepitaxial growth rate on substrate temperature at a methane mole
fraction of 0.4% for growth on (100) (squares), (110) (diamonds), and (111) (triangles)
orientations. CH_4 was injected above the filaments.