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D. Zhou

T. G. McCauley

L. C. Qin

A. R. Krauss

D. M. Gruen

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Synthesis of nanocrystalline diamond thin films from an Ar-CH₄ microwave plasma

D. Zhou,^{a)} T. G. McCauley, L. C. Qin, A. R. Krauss, and D. M. Gruen

Materials Science and Chemistry Divisions, Argonne National Laboratory, Argonne, Illinois 60439

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Nanocrystalline diamond thin films have been synthesized in an Ar-CH₄ microwave discharge, without the addition of molecular hydrogen. X-ray diffraction, transmission electron microscopy, and electron energy loss spectroscopy characterizations show that the films consist of a pure crystalline diamond phase with very small grain sizes ranging from 3 to 20 nm. Atomic force microscopy analysis demonstrates that the surfaces of the nanocrystalline diamond films remain smooth independent of the film thicknesses. Furthermore, the reactant gas pressure, which strongly affects the concentration of C₂ dimer in the Ar-CH₄ plasma as well as the growth rate of the films, has been found to be a key parameter for the nanocrystalline diamond thin film depositions.

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I. INTRODUCTION

Atomic hydrogen has long been recognized as playing a crucial role in the growth of polycrystalline diamond films by chemical vapor deposition (CVD), typically using hydrocarbons as the carbon source.¹⁻³ It is well known that atomic hydrogen from a hydrogen-rich reactant gas can terminate the carbon dangling bonds with a tetrahedral *sp*³ configuration and etch out nondiamond materials at the growth surface of diamond during the CVD film depositions.⁴⁻⁶ Reducing the concentration of atomic hydrogen or increasing the concentration of hydrocarbons in the reactant gas (or plasma) normally causes either nondiamond phase growth or no diamond film deposition.^{7,8} On the other hand, the grain sizes and the surface roughness of the polycrystalline diamond films prepared from a hydrogen-rich plasma depend heavily on the film thickness. Generally, the thicker the film, the bigger the grain size and the rougher the surface of the film.

In order to increase the electron density of the plasma and to modify diamond film morphology, argon has been added independently to plasmas.⁹ Furthermore, argon has also been used in place of hydrogen in a carbon-oxygen-argon system, but oxygen was a critical parameter for the phase purity of the deposited diamond films.¹⁰ Recently, Gruen *et al.* has reported that nanocrystalline diamond thin films can be grown from an Ar-C₆₀ microwave plasma without adding molecular hydrogen to the reactant gas.¹¹ In Gruen's experiments, fullerenes, such as C₆₀ and C₇₀, have been successfully used as the carbon source for the diamond growth. Through an argon microwave plasma fragmentation of fullerenes (without hydrogen involved), the discharge displays a strong green color (Swan band) due to the 5165 Å emission from the C₂ radicals, and the C₂ dimer appears to be the growth precursor of nanocrystalline diamond.^{12,13} Note that the nanocrystalline diamond thin films prepared from an Ar-C₆₀ microwave plasma with C₂ dimers as the

growth precursors have their own unique properties, such as nanocrystalline diamond grains, exceptionally smooth as-grown surfaces, and outstanding electron field emission properties.^{14,15} The growth of nanocrystalline diamond thin films using hydrocarbon as the growth precursors in a plasma enhanced CVD system without hydrogen or oxygen addition, however, appears not to have been studied in detail.¹⁶

We report here on the growth of nanocrystalline diamond thin films from an Ar-CH₄ microwave plasma without the addition of molecular hydrogen or oxygen. X-ray diffraction (XRD), transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS) analyses demonstrate that the as-grown films from the Ar-CH₄ plasma consist of phase-pure crystalline diamond grains ranging from 3 to 20 nm in size independent of the film thickness. Similar to the nanocrystalline diamond films prepared from Ar-C₆₀ plasmas, the nanocrystalline films synthesized from Ar-CH₄ plasmas also have very smooth surfaces. Based on the study of the optical emission of C₂ dimer from the Ar-CH₄ plasmas and the growth rates of the films at different pressures ranging from 55 to 150 Torr, we demonstrate that increasing reactant gas pressure enhances strongly the concentration of C₂ in the plasmas, and thus significantly promotes the growth of nanocrystalline diamond thin films.

II. EXPERIMENTS

A mixture of Ar (99 sccm) and CH₄ (1 sccm) was employed as the reactant gas for the microwave plasma enhanced CVD thin film preparations. *N*-type single crystal silicon wafers with ⟨100⟩ orientation were used as the substrates, and mechanical polishing with fine diamond powder (0.1 μm) was employed to enhance the nucleation density. For all film depositions the substrate temperature and input microwave power were maintained at 800 °C and 800 W, respectively. The films prepared in this work were either 1 or 5 μm thick, as determined by using an *in situ* laser reflectance interferometer to monitor the modulations of the surface reflectivity during the growth process.¹⁷ To study the dependence of growth rate of the film on C₂ concentration in the plasma, the reactant gas pressure, which strongly affects

^{a)}Current address: Advanced Materials Processing and Analysis Center, Dept. of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, FL 32816.
Electronic mail: dzhou@pegasus.cc.ucf.edu

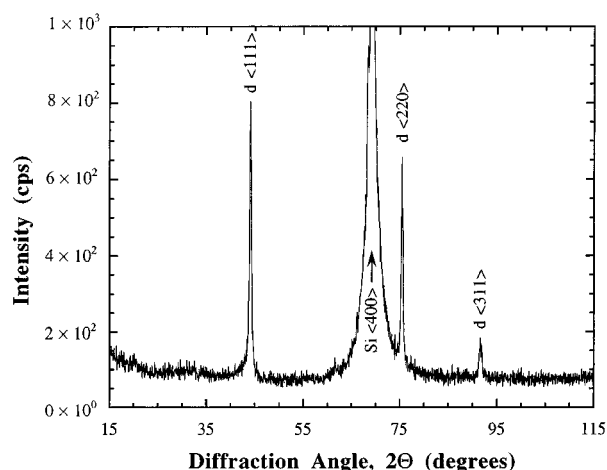


FIG. 1. X-ray diffraction of the as-grown nanocrystalline diamond film prepared from an Ar-CH₄ plasma at 100 Torr. The labels show the diffraction peaks from different planes of the cubic diamond.

production of C₂ dimers from the Ar-CH₄ plasmas, was varied from 20 to 150 Torr. A spectrometer equipped with a 1200 GR/mm grating and water-cooled photomultiplier tube was employed to monitor the Ar-CH₄ plasma, and specially the concentration of C₂ dimers. Emission from the plasma was collected with a quartz optical fiber viewing a region 1–2 cm above the substrate. The monochromator was stepped in 2.3 Å increments with a dwell time of 100 ms from 3000 to 7000 Å. The characterization of the as-grown films was then carried out using XRD, TEM, EELS, and atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

The x-ray diffraction spectrum of the as-grown film is shown in Fig. 1. The diffraction peaks can be indexed on the basis of the cubic diamond structure (see the labels in Fig. 1). The diffraction peaks are significantly broadened due to the very small grain sizes. There is no evidence for graphite or amorphous carbon from the x-ray diffraction. The silicon diffraction peak from Si {400} planes derives from the substrate used for the film deposition. Further characterization of the films has been conducted using TEM. Figure 2(a) shows a plan view TEM image, showing that the film contains very small grains ranging from 3 to 20 nm, but the actual size can be determined more accurately from high resolution TEM images.¹⁸ The inset image shows a selected area (over 10 μm in diameter) electron diffraction of the film, in which the sharp ring pattern illustrates that the diamond grains have a random orientation. EELS was employed as a diagnostic for amorphous or disordered carbon with *sp*² bonding. It is known that different carbon phases (graphite or amorphous carbon and diamond) have very distinct *K*-shell absorption edge structures. Diamond has a single EELS feature with an onset at 289 eV due to its σ^* electronic states, while graphite or amorphous carbon has an additional EELS edge starting at 284 eV owing to its lower lying antibonding π^* states.¹⁹ Figure 2(b) shows an EELS spectrum of the nanocrystalline diamond film acquired over an area ~10 μm in diameter, displaying only an EELS edge at 289 eV, characteristic of

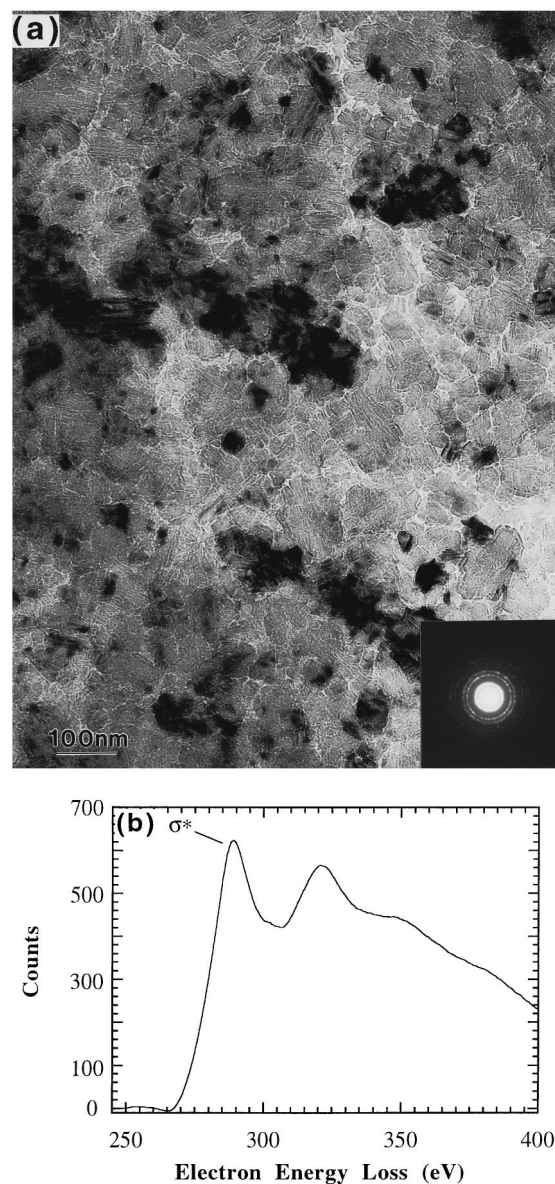


FIG. 2. (a) A plan view TEM image of the diamond film prepared from an Ar-CH₄ plasma at 100 Torr showing that the diamond film consists of nanocrystalline grains ranging from 3 to 20 nm. The inset image shows a sharp ring pattern of a selected area electron diffraction, indicating that the diamond grains have a random orientation; (b) an EELS spectrum of the nanocrystalline diamond film acquired over an area ~10 μm in diameter, displaying only an EELS edge at 289 eV corresponding to a *sp*³ electron configuration, characteristic of diamond.

diamond. No energy loss feature at 284 eV has been observed, demonstrating the absence of amorphous or graphite phases in the film. A high resolution TEM image of the nanocrystalline thin film shown in Fig. 3 demonstrates that individual grains are single diamond crystals. The image of lattice fringes has a spacing of 0.205 nm, which is the interplanar distance between diamond {111} planes. The lattice image of diamond can only be observed when the diamond {111} planes are in proper orientation since the resolution of the TEM used is about 1.8 Å.

The surface morphologies of the as-grown nanocrystalline diamond thin films have been studied by AFM. Figure 4 shows three-dimensional AFM images of the films with dif-

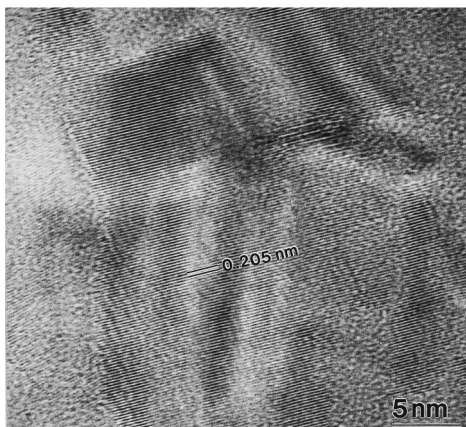


FIG. 3. A high resolution TEM image of the nanocrystalline diamond film produced from an Ar-CH₄ microwave plasma at 100 Torr showing the lattice image of the diamond nanocrystals.

ferent thicknesses of (a) 1 μm and (b) 5 μm , illustrating that the films produced from the Ar-CH₄ plasma have very smooth surfaces. The surface roughness measured over an area of 5 μm \times 5 μm for these two films are 36.5 and 38.6 nm, respectively, suggesting that the surface roughness of the nanocrystalline diamond films is largely insensitive to the

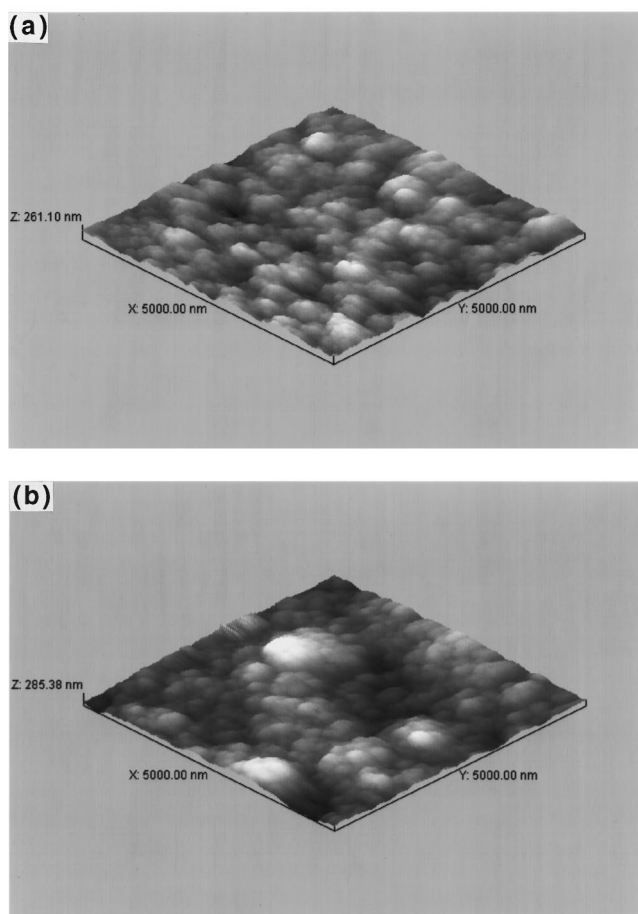


FIG. 4. Three-dimensional AFM images of the films with different thicknesses of (a) 1 μm and (b) 5 μm , illustrating that the nanocrystalline diamond thin films produced from the Ar-CH₄ plasma have very smooth surfaces, which appears to be independent of the film thicknesses.

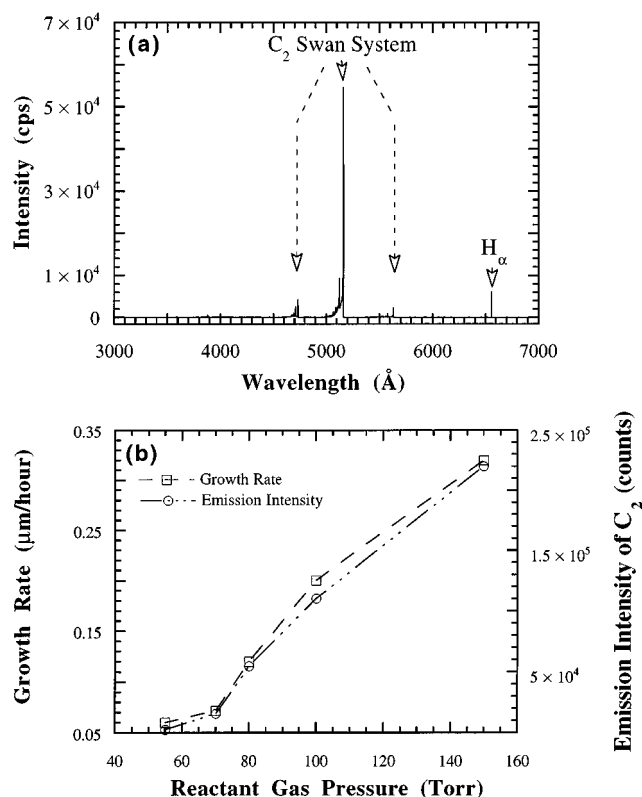


FIG. 5. (a) An optical emission spectrum of the Ar-CH₄ plasma running with 1 vol % CH₄ and 99 vol % Ar as the reactant gas at a chamber pressure of 100 Torr; (b) plots of growth rates of nanocrystalline diamond films and emission intensities of C₂ from the Ar-CH₄ plasmas vs reactant gas pressures ranging from 55 to 150 Torr.

film thickness, which is in contrast to the conventional CVD polycrystalline diamond films prepared by an atomic hydrogen-rich microwave plasma. Therefore, a new growth precursor such as C₂ dimer associated with a novel growth mechanism should be considered for the nanocrystalline diamond thin film deposition from an Ar-CH₄ plasma presented here.

To obtain information from the Ar-CH₄ plasmas, optical emission spectroscopy was employed. Figure 5(a) shows a typical emission spectrum of the Ar-CH₄ plasma running with 1 vol % CH₄ and 99 vol % Ar as the reactant gas at the chamber pressure of 100 Torr. In this spectrum, the C₂ swan system (5165 Å bands) has been observed through in the wavelength range from 3000 to 7000 Å. A weak emission line of H_α (6562 Å) from atomic hydrogen, which is contributed by the discharge reaction of methane, is also visible in this emission spectrum. Figure 5(b) shows plots of growth rates of nanocrystalline diamond films and emission intensities of C₂ from the Ar-CH₄ plasmas versus reactant gas pressures ranging from 55 to 150 Torr, showing that the pressure strongly affects both the Ar-CH₄ discharge chemistry and the nanocrystalline diamond film growth. The growth rates of nanocrystalline thin films deposited from the Ar-CH₄ plasmas are determined by monitoring modulations of the surface reflectivity versus deposition time with a He-Ne laser (6328 Å) reflectance interferometer.¹⁷ One modulation (from peak to peak) presents a film deposition

130 nm thick. The emission intensities of C_2 , which correlates linearly with the absolute C_2 concentration in Ar- CH_4 microwave plasmas,²⁰ are directly measured from the C_2 swan system (5165 Å bands) in the optical emission spectra. When the reactant gas pressure is below 40 Torr, no C_2 emission is detected by our optical emission spectrometer, and no diamond film growth is observed. Similarly, diamond film growth is not observed from Ar- CH_4 plasmas up to 15 Torr.²¹ At 55 Torr, a very low emission intensity of C_2 is seen [Fig. 5(b)], and is accompanied by a correspondingly low growth rate of the nanocrystalline diamond thin film is about 0.06 $\mu\text{m/h}$. As the reactant gas pressure increased, both the emission intensity of C_2 dimers and the growth rate of the films are increased significantly [see Fig. 5(b)]. Note that the linear relationship between the growth rate and the C_2 concentration shown in Fig. 5(b) suggests that the concentration of C_2 in the Ar- CH_4 plasma is the factor determining the film growth rate.

Our observations demonstrate that the reactant gas pressure plays an important role in enhancing the emission intensity and therefore the concentration of C_2 in Ar- CH_4 plasma. That C_2 is the growth species for nanocrystalline diamond is confirmed by the functional relationship between the C_2 concentration and the growth rate. Although the C_2 dimer can be efficiently produced by Ar- CH_4 discharges, the fragmentation of C_{60} molecules in an Ar microwave plasma producing C_2 appears to be even more efficient as a result of high cross sections for dissociation by metastable argon atoms, by charge exchange with argon ions, by dissociative recombination with electrons, and by thermal processes.²² TEM analysis reveals that diamond thin films produced from Ar- CH_4 discharges consist of very small grain sizes ranging from 3 to 20 nm, indicating that renucleation rates must be very high. The very high renucleation rates, which result in nanocrystalline diamond rather than graphite in an Ar- CH_4 plasma, suggest that during the deposition process nucleation of the diamond phase occurs in the absence or near absence of atomic hydrogen.

IV. CONCLUSIONS

Nanocrystalline diamond thin films have been synthesized by microwave plasma enhanced CVD using a mixture of Ar and CH_4 as the reactant gas without any molecular hydrogen addition. The films consist of a pure nanocrystalline diamond phase with grain sizes ranging from 3 to 20 nm. The films produced from an Ar- CH_4 microwave plasma have very smooth surfaces, which do not depend on the thickness (at least in the range of 1–5 μm) of the film. The reactant gas pressure has been demonstrated to play a very important role in enhancing the concentration of C_2 in the plasma, which in turn controls the growth rate. The depen-

dence of the growth rates of the nanocrystalline diamond films on the optical emission intensities for the C_2 dimer in the plasma supports the mechanism of nanocrystalline diamond growth from C_2 dimers proposed by Gruen *et al.*^{11,12}

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