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Thin Solid Films 335 (1998) 27–31

thin solid films

Growth and characterization of diamond-like carbon films by pulsed laser deposition and hydrogen beam treatment

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Received 19 November 1997; accepted 1 May 1998

Abstract

Amorphous diamond-like carbon films have been grown by pulsed laser deposition using a graphite target both with and without an atomic hydrogen beam incident on the growing film. Films grown with the hydrogen beam showed resistivity nearly two orders of magnitude higher than the films grown without hydrogen. Raman scattering confirmed a higher degree of sp^3 bonding in films exposed to hydrogen atoms during growth. Films grown without hydrogen but exposed to the hydrogen beam after growth showed a significant increase in resistivity after exposure. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Carbon; Hydrogen; Laser ablation; Resistivity

1. Introduction

The role of hydrogen in diamond film growth is uncertain, but it seems to be necessary for the growth of the highest quality diamond films. In a chemical vapor deposition (CVD) process, for example, feed gases are often 95–99.5% H_2 with the balance being methane. Various possible roles have been postulated for atomic hydrogen in the growth of diamond films and diamond-like carbon (DLC) films; these include preferential etching of graphitic rather than diamond centers and stabilization of the sp^3 diamond-like bond [1,2]. There is some evidence that hydrogen improves film quality in other diamond growth methods besides the CVD studies with hydrocarbons [3,4]. Kelly et al. [5] grew diamond films by alternately exposing their substrates to flux from a graphite sputtering target and to flux from H_2 flowed past a hot filament. Jubber et al. [6] increased the resistivity of their CVD diamond films by as much as nearly four orders of magnitude (from 48 to 2.2×10^5 Ω cm) by post-growth exposure to a hydrogen atomic beam.

Pulsed laser deposition (PLD) as a method for depositing amorphous carbon (a-C) and diamond-like carbon (DLC) was pioneered by Marquardt et al. [7] and recently has been reviewed by Voevodin and Donley[8]. PLD has the advantage that DLC films with a large percentage of sp^3 bonding can be grown with the substrate at or near room-temperature, while the diamond films grown by CVD require growth temperatures ~800–1100°C. The lower growth temperature makes these DLC films attractive for numerous applications. The goal of the work reported here is to determine whether the sp^3 content of the low temperature films can be increased by exposure to hydrogen atoms.

Previous studies of the effect of hydrogen in the PLD of DLC have been inconclusive. Two groups [9,10] reported DLC films grown in a hydrogen atmosphere showed increased optical band-gaps. Thebert-Peeler et al. [11], however, reported that hydrogen had no effect on DLC film quality.

In this study, an atomic beam of hydrogen was directed onto silicon and sapphire substrates either simultaneously with or subsequent to the flux of carbon that was laser ablated onto these substrates. The properties of these films were studied by atomic force microscopy (AFM), resistivity measurements, and Raman scattering.

2. 0 Experimental procedure

The deposition was performed in an ion-pumped chamber with a base pressure of 6.7×10^{-9} mbar (5×10^{-9} Torr). A Lambda Physik Lextra 100 KrF (248 nm) excimer laser was operated at 250 mJ at repetition rates of 1, 2, and 6 Hz and focused to produce a maximum power density of 1×10^9 W/cm^2 at the target (UNOCAL POCO graphite), which was

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0040-6090/98/$ - see front matter
PII S0040-6090(98)00867-0

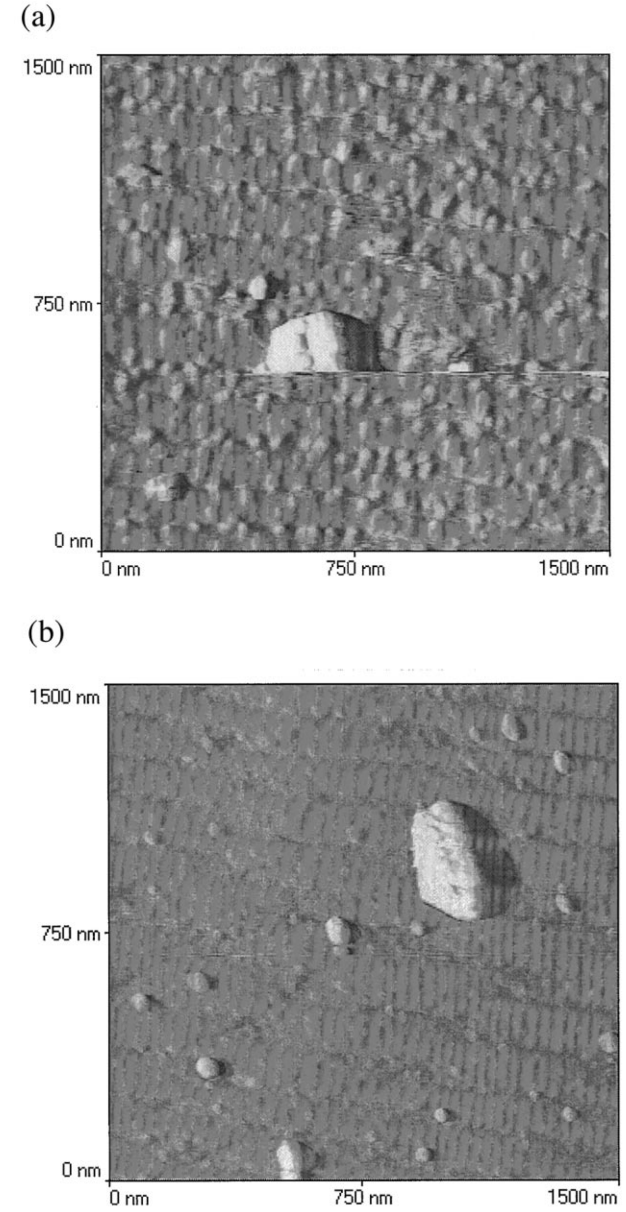

Fig. 1. AFM images of carbon films grown (a) without H beam and (b) without H beam during growth but with 3 h post-growth H beam exposure.

rotated at slightly less than 2 Hz. Films were deposited at room temperature on 0.5 × 0.5 cm etched silicon and sapphire substrates.

Also incident on these substrates was an effusive atomic hydrogen beam created by microwave plasma dissociation of hydrogen gas. Up to 120 W continuous wave was supplied to a 2.45-GHz resonator cavity, and this power was transferred to a discharge tube holding 1 Torr of H_2. The tube was cooled to approximately 220K to minimize hydrogen atom recombination [12]. Conditions were optimized to maximize the intensity of the Balmer α-line by using optical emission spectroscopy.

Films were grown either without hydrogen impingement, with H-atom simultaneous flux, with H-atom post-growth flux of 3 h duration, or with H_2 flux (i.e. no plasma). The laser was fired for a total of 9000 shots regardless of repetition rate and produced films of 1200 Å nominal thickness.

Topography was studied using a Topometrix TMX2000 AFM system. Experiments were performed in air ambient conditions in the contact mode. The system contained programs to calculate rms roughness and particle size and density.

The resistivity was measured for the films grown on sapphire using the four-point probe technique. The silicon substrates were more conductive than the DLC films by 2–5 orders of magnitude so resistivity measurements were not made for films grown on silicon. Resistivity of the more conductive films ($<10\ \Omega$ cm) was measured on a Veeco FFP-100 four-point probe station. This instrument has four sharp tips which penetrate the film and the substrate. For the more resistive films, gold strips were evaporated onto the film, and silver paste was used to bridge the contact from the gold to the measuring electrodes. Resistivities for films which were measured by both methods were in numerical agreement.

The films were analyzed by Raman scattering in the range from 1100 to 1800 cm^{-1} using an argon (514 nm) laser at a power of 1 W and a spot size of 0.2 cm^2. The spectra of the films grown on sapphire could not be easily interpreted since the scattering signal was buried underneath the fluorescence induced by the sapphire.

3. Results and discussion

3.1. Film morphology

The films were a uniform light-brown in color and varied by no more than 10% in thickness from point-to-point on a sample. The results of microscopic observation were also relatively independent of the region studied for a given sample. AFM images are displayed in Fig. 1. Both films exhibit graphite particulates ejected from the target, a well-known phenomenon in PLD growth [13]. The particles would be expected to be located nearer to the surface of the film because target quality degrades as deposition proceeds. It is apparent that particles are more numerous and larger on average in the film without hydrogen treatment. This could be due to etching of the particles by the atomic hydrogen beam. A simple calculation can be made to determine the time that it would take to etch a spherical graphite particle. We assume 10^{-2} graphite atoms are removed for each incident hydrogen atom using the data of Donnelley et al. [14] for the conditions of the present experiment. Assuming complete H_2 dissociation, the hydrogen atom flux from the source under normal operating conditions is estimated to be $\sim 2 \times 10^{15}$ atoms/s per cm^2 from calculations of the intensity of a molecular beam from an effusive source [15]. Under these conditions a spherical surface particulate of ~ 17 nm diameter would be completely etched in the three

Table 1
Room-temperature resistivity of C films grown by pulsed laser deposition (Ω cm)[a]

	No H	w/H	H post growth only
No. of samples	3	3	3
Mean	0.42	14	1.2
Standard deviation	0.29	2.5	0.7

[a] For comparison, the measured resistivity of the graphite targets used in these experiments was 3.8 mΩ cm and room-temperature resistivities of DLC films are typically in the range from 10^{-1} to 10^{8} Ω cm depending on growth parameters [26].

hours that we ran the hydrogen source. However, if either the assumed etch rate or our estimate of hydrogen flux is too small by a factor of two, it would mean that a ~35 nm diameter particle would be completely etched away and a ~50 nm diameter particle would be reduced to ~40 nm in diameter. The latter figures are typical of the size of particles in Fig. 1a so an etching of particles by the post-growth hydrogen beam is indeed plausible.

Although the film grown without hydrogen has more particles, its root mean square (rms) roughness is actually smaller than the etched film – 11.95 nm compared to 18.83 nm. For a smaller scan (200 × 200 nm) away from large particles, the difference becomes more pronounced – 1.86 nm compared to 3.45 nm. The roughening of the surface of the post-growth hydrogen treated film is very likely due to sp^2 regions of the surface being etched while sp^3 regions are left behind since graphite is etched several orders of magnitude faster than diamond [14].

3.2. Resistivity

The results of four-point probe measurements are shown in Table 1. It is apparent that the use of the atomic hydrogen beam significantly increased the resistivity of the carbon films. Films grown with simultaneous hydrogen flux were nearly two orders of magnitude more resistive than films grown without the hydrogen source. Films subjected to hydrogen flux for three hours immediately after growth but not during growth showed an increase in resistivity by a factor of approximately 3. This latter trend is in qualitative agreement with the Jubber et al. study [6] of atom beam treatment of diamond films and could result from the etching of surface graphite layers which typically form on films with high sp^3 content [6].

As a control, a sample was grown in which the microwave plasma was turned off, and hydrogen molecules were directed onto the substrate during growth. This sample had the same resistivity as a sample grown under the same conditions except without hydrogen. This demonstrates that hydrogen atoms rather than hydrogen molecules are responsible for changing the electrical properties of the diamond-like films.

From Dektak profilometer thickness measurements, the time averaged carbon flux is $\sim 1 \times 10^{14}$ atoms/s per cm^2 for a 1-Hz laser repetition rate. This corresponds to a monolayer coverage every 5–10 pulses assuming unity incorporation coefficient, so that hydrogen can presumably etch sp^2 bonded carbons or stabilize sp^3 bonded carbons in between pulses given our above estimate of $\sim 2 \times 10^{15}$atoms/s per cm^2 for the flux of hydrogen.

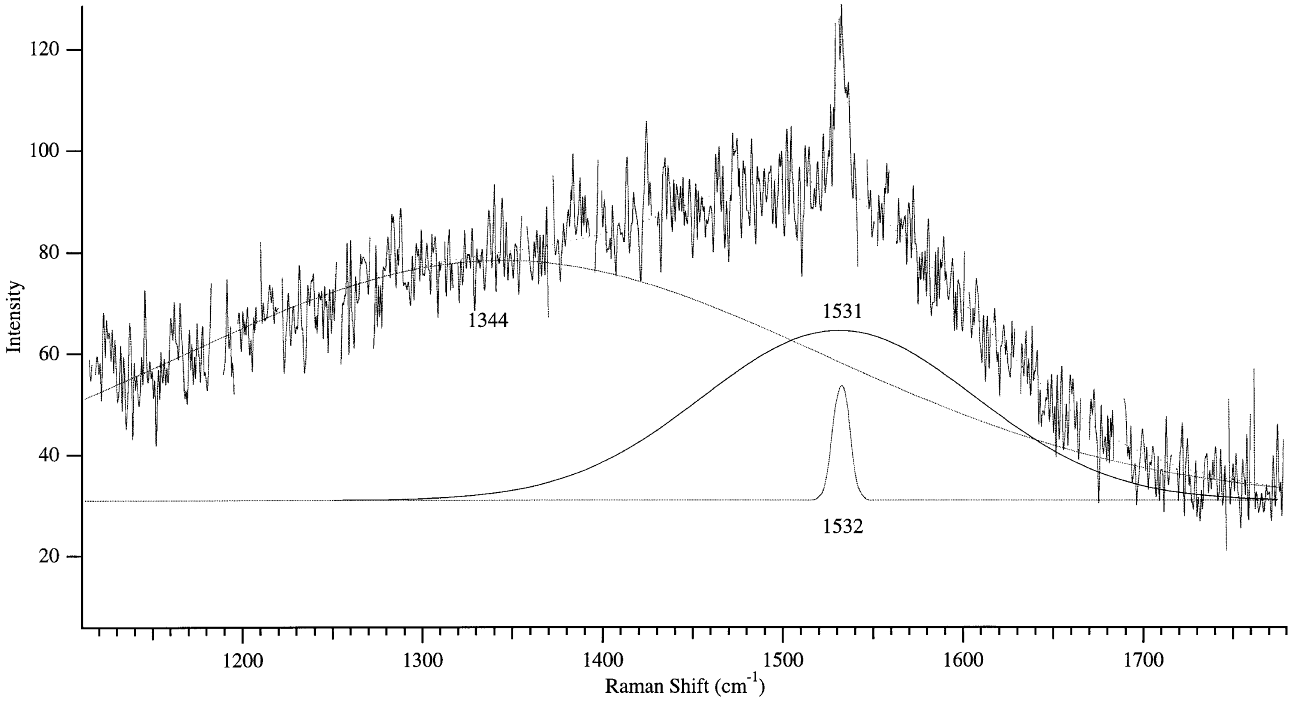

Fig. 2. Raman spectrum of film grown without H beam. Fit with Gaussians.

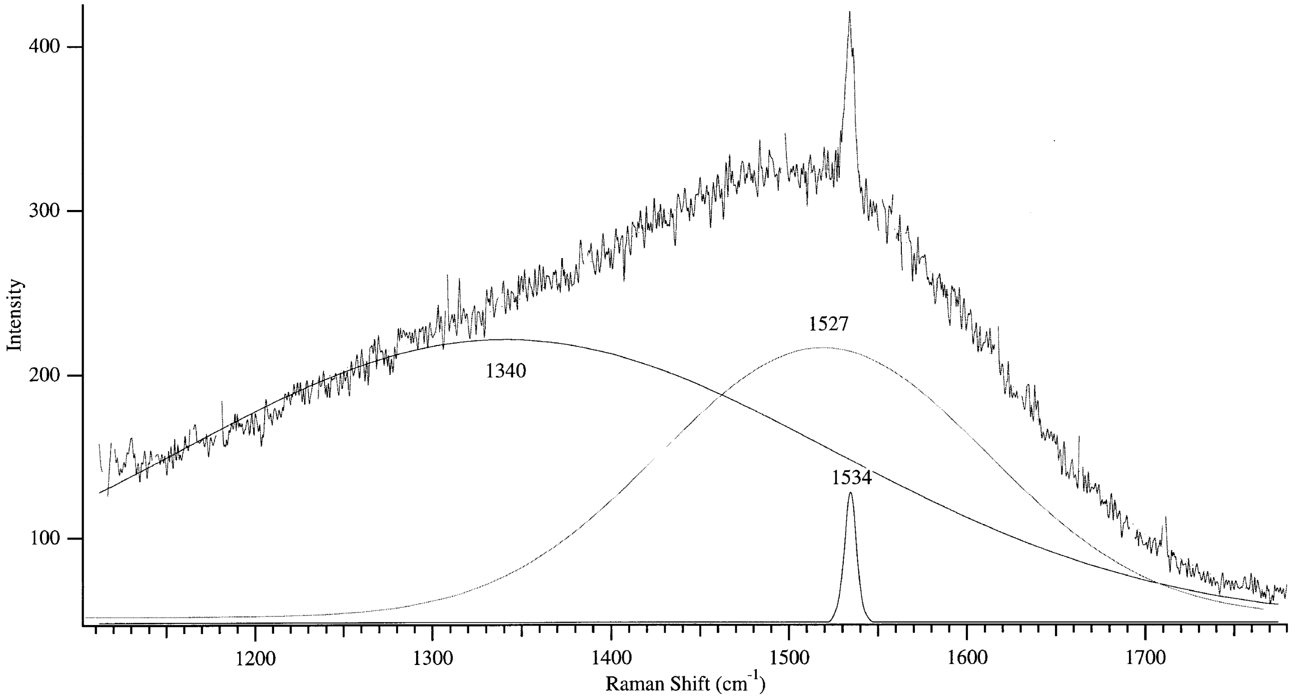

Fig. 3. Raman spectrum of film grown with H beam. Fit with Gaussians.

One widely accepted model for DLC formation at low temperature from moderate energy flux is the subplantation model [16,17]. In this model carbon flux is implanted in near surface layers causing an increase in local density which leads to rehybridization to sp^3 bonding. Ions or neutrals with lower energies stick to the surface in an sp^2 configuration. Ions with excess energy cause lattice vibrations or mobile defects leading to density relaxation through atoms migrating to the surface [18]. Since the surface in this model is sp^2, our resistivity increase would then be due to an etching and regrowth mechanism rather than a hydrogen-assisted stabilization of sp^3 centers. However, we observed no significant difference in thickness for films grown with hydrogen as one might expect from films that are etched a great amount. According to a different model [19], sp^3 centers may also form at the surface during PLD growth. In this situation, the sp^3 centers might be thermodynamically stabilized by the hydrogen flux as they form. Further work with broader ranges of hydrogen and carbon fluxes is needed to quantify this data and elucidate the mechanism of resistivity increase.

3.3. Raman scattering

Raman spectra of samples grown on silicon without and with simultaneous hydrogen flux are presented in Figs. 2 and 3, respectively. The spectra are fitted with three Gaussian functions. The broad Gaussian at ~1530 cm^{-1} corresponds to the G (G for graphite) peak and is due to the Raman allowed E_{2g} mode [20]. The G peak position varies from 1520 cm^{-1} for amorphous carbons to 1590 cm^{-1} for glassy carbons [21] and has been shown to be in the lower end of this range for films with higher sp^3 content [22]. The D (D for disordered) peak is due to a peak in the phonon density of states of graphite and can be observed when the crystallite size is small enough that the $k = 0$ selection rule is relaxed [22,23]. The narrow Gaussian peak has, to the best of our knowledge, not been observed before in amorphous carbon films. This peak could be the result of the ejection of graphite particulates from the target during deposition since Raman spectra of graphite films typically have a peak with a similar full width at half maximum [20,24] although generally at a higher wavenumber. In analyzing all our spectra, we found that the narrow peak, to a great extent, varied directly with measured resistivity and particulate density. Also, the Raman spectrum of the target contained a large sharp peak at ~1530cm^{-1} rising from a broader peak centered at about the same place lending support to the hypothesis that the peak is a target particulate effect.

In comparing Figs. 2 and 3, we looked at several parameters that are commonly used to judge diamond-like quality of a film. For example, we see that the broad G and D peaks are slightly downshifted for the sample grown with hydrogen compared to the sample grown without hydrogen. Downshift in D and G peaks has been correlated with increased sp^3 percentage [22,25–27]. Also, the ratio of the intensity of the D peak to the intensity of the G peak (I_D/I_G) goes from 3.4 to 2.1. This indicates increased sp^3 character and reduced graphite crystallite size within the amorphous matrix for the film grown with hydrogen bombardment [18,27]. Finally, the width of the broad G peak is greater in the film grown with hydrogen suggesting the film is becoming more amorphous and less dominated by graphite microcrystals [18,25,27]. Each of these parameters are fingerprints which consistently show our films grown with hydrogen to be more diamond-like and less graphitic than those which we grew without hydrogen.

4. Conclusion

DLC films grown by PLD in the presence of atomic hydrogen have dramatically higher resistivity than films grown without hydrogen. Structurally, this difference is corroborated by substantially greater sp^3 character in films grown with hydrogen, as determined by Raman spectra. These results demonstrate that PLD has the potential to grow very high-quality DLC films at low temperatures if the films are exposed to H atoms during growth. The detailed mechanism of H-assisted growth remains to be elucidated.

Acknowledgements

The authors wish to thank P.A. Steiner IV for technical assistance in setting up the hydrogen atom source. This work was supported by the National Science Foundation (grant no. DMR 92-02879) and by the Office of Naval Research (grant no. N0001492J1718).

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