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Conf-940411--34

BNL-60467

ATOMIC STRUCTURE MODIFICATIONS OF DIAMOND-LIKE NANOCOMPOSITE FILMS: OBSERVATION BY RAMAN SPECTROSCOPY, FTIR AND STM

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ABSTRACT

Raman spectroscopy, FTIR and scanning tunneling microscopy (STM) were used to study diamond-like nanocomposite (DLN) and metal containing DLN (Me-DLN) films. The FTIR spectra showed no appreciable absorption from the C-H stretch vibration band in DLN when 1 kV rf bias voltage was applied. Thermal annealing (450°C for 2 hrs) of (a) DLN and Cr-DLN films caused no change in the Raman spectra while (b) for Pt-DLN films there was a blue shift of both the crystalline (G) and microcrystalline (D) graphite-like features, an increase in the I_D/I_G intensity ratio and a decrease in the linewidths. The changes observed were more pronounced in the film with the highest Pt concentration. The STM image of this Pt-DLN film revealed a structure of aromatic graphite rings.

INTRODUCTION

During the last decade several kinds of carbon with novel structure and properties have been developed. Diamond-like carbon (DLC) films represent one of these innovative materials which possess many of the technologically important properties of diamond, such as hardness, high chemical stability, wear resistance, high electrical resistivity and high thermal conductivity [1-4].

The development of amorphous diamond-like nanocomposites (DLN) and metal containing DLN (Me-DLN) has been described previously [5-8]. It was shown that these materials possess unique combinations of mechanical, chemical, optical, electronic and superconducting properties. The introduction of transition metals makes it possible to change the electrical resistivity over 18 orders of magnitude (between about 10^{15} ohm-cm to $2\text{-}4\times10^{-4}$ ohm-cm). It has been established earlier that doping of DLN with tungsten [7] as well as other high melting temperature transition metals leads to stability enhancement. However, it was also suspected that noble metals affect the basic matrix and cause a decrease in the stability of the film. The aim of this investigation is to determine the effect of the metal type on the thermal stability of composites of atomic scale. This comparison study was carried out using Cr as a transition metal and Pt as a noble metal.

EXPERIMENTAL DETAILS

DLN films were deposited in a high frequency field (1.76 MHz) from a plasma discharge (plasma current 1-4 A, voltage 150 V) of polyphenilmetilsiloxane

$[(C_2H_5)_3SiO[CH_3C_6H_5SiO]_3Si(CH_3)_3]$. The Cr-DLN and Pt-DLN films were synthesized in a combined process of DLN deposition and *dc* magnetron sputtering of the metal target (400-500 V, 0.2-2.0 A in Ar). The <100> Si substrate wafers were cleaned *in situ* by Ar plasma etching prior to deposition. The thicknesses of the DLN, Cr-DLN and Pt-DLN films were in the range 0.2-1.0 μm, 0.7-1.2 μm, and 0.7-1.2 μm, respectively. The sheet resistance (ρ_s) of the Cr-DLN was 1800 $\Omega/\Box$. Two types of Pt-DLN films were studied: samples A and B with $\rho_s = 1500\ \Omega/\Box$ and $\rho_s = 1\mathrm{x}10^6\ \Omega/\Box$, respectively. Some films were annealed in vacuum at 450°C for 2 hrs.

The Fourier Transform Infrared (FTIR) spectra were taken with a Mattson Cygnus 100 with DTGS detector. The Raman measurements were made using the 515 nm, 488 nm, or 475 nm lines of an Ar-ion laser as an excitation source. The laser power on the sample was about 1 Watt. No change in the lineshape with respect to laser intensity was found. All measurements were taken in the backscattering geometry. The instrumental resolution was about 6 cm^{-1}.

The Raman spectra, $I(\omega)$, were fitted by an equation which contains a low frequency, aymmetric (D) and a Lorentzian (G) term [12]:

$$I(\omega) = I_0 + I_D \cdot \frac{(2/\pi)(\Delta\omega_D)\omega_D^2}{(\omega^2-\omega_D^2)^2+(\Delta\omega_D)^2\omega^2} + I_G \cdot \frac{(1/\pi)(\Delta\omega_G)}{(\omega-\omega_G)^2 + (\Delta\omega_G)^2} \tag{1}$$

where I_0 is the background, I_i is the integrated intensity, ω_i is the peak position and $\Delta\omega_i$ is the full width at half maximum of the i^{th} feature, respectively.

All STM images were taken in the constant current mode, with the set current around 1 nA and the tip bias voltage around -200 mV (tip negative with respect to the sample). STM tips were mechanically formed from Pt90/Ir10 wires.

EXPERIMENTAL RESULTS

The FTIR spectra of as-deposited DLN films formed at different rf bias voltages (V_{rf}) are displayed in Fig 1. No arbitrary scaling factors were introduced and curves are displaced for clarity. It can be seen that an increase from $V_{rf} = 0$ to $V_{rf} = 1000$ V causes the disappearance of the broad C-H stretching vibration band at 2900 cm^{-1} [9,10] and a considerable decrease of the peaks at 1600 cm^{-1} (C=C sp^2 stretching vibrations [11]) and 1000 cm^{-1}. The nature of this latter feature is not clear. However, the complete absence of the C-H stretch vibration causes us to believe that the properties of this film are not conditioned by hydrogen incorporation. After thermal annealing the film with $V_{rf} = 0$ was destroyed. Annealing the films deposited with $V_{rf} = 300$ V and $V_{rf} = 1000$ V did not change significantly the peak intensities but it did increase film transparency.

Figure 2 shows the FTIR spectra of the various Pt-DLN films. The spectrum of sample A is less transparent in relation to sample B because of the higher metal concentration (the correlation between ρ_s and metal concentration is presented in [8]). Thermal annealing of the Pt-DLN films causes some increase in the intensity of the peak at 1600 cm^{-1}. The appearance of the 1600 cm^{-1} peak after annealing at 390°C was observed by Grill et al.[11], and explained as the organization of the carbon atoms in the graphite coordination. The FTIR spectrum of Cr-DLN remained almost unchanged after annealing and is similar to that of as-grown sample A.

The first order Raman spectra for both crystalline forms of carbon, i.e., graphite (with threefold coordination symmetry) and diamond (with fourfold coordination symmetry) are well known [12,13]. The first order Raman spectrum of diamond consists of a single sharp line at

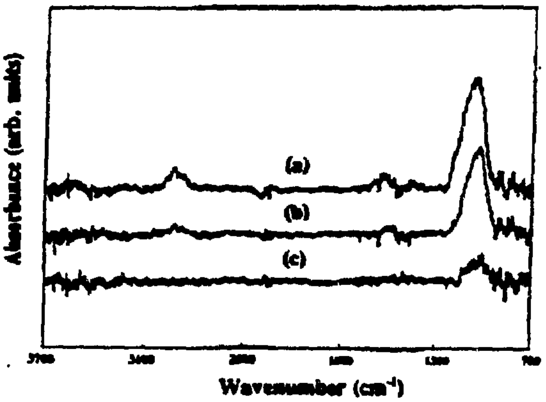

Fig. 1 FTIR spectra of DLN films formed with V_{rf} = (a) 0 V, (b) 300 V and (c) 1000 V.

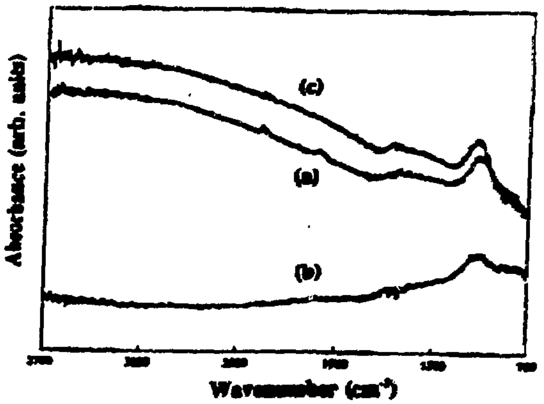

Fig. 2 FTIR spectra of Pt-DLN films (a) sample A, as-deposited, (b) sample B, as-deposited and (c) sample A, annealed.

1332 cm^{-1} while that of graphite (G) shows a single peak at 1580 cm^{-1}. In addition to the G feature the Raman spectrum of microcrystalline graphite contains a line (D) at about 1355 cm^{-1}, which is due to the relaxation of the q = 0 selection rule [12,13]. The first order Raman spectra (solid lines) at 300K of as-grown and annealed DLN and Pt-DLN (sample A) are presented in Figs. 3 and 4, respectively. The dotted lines are the fitted curves from Eq. (1) for the D and G structures individually while the dashed lines are the sum of the two contributions. Table I lists the parameters of the Raman spectra (integrated intensity ratios, peak positions and widths) obtained from the fit. The Raman spectrum of the Cr-DLN film was similar to that of sample A but remained unchanged after annealing.

The important features of the spectra are (a) similar broad asymmetric two-component peaks, (b) almost no change in the spectra of DLN and Cr-DLN (not presented in this article) after annealing and (c) annealing of the Pt-DLN films produces an upward shift of the G and D line positions, a decrease in their linewidths and an increase in the ratio I_D/I_G. The computer model of Beeman et al.[14] predicts a downshift in the frequencies of both the D and G lines as a result of bond-angle disorder and some fourfold coordination. This prediction seems close to the average peak positions observed in the DLN and Cr-DLN films and as-grown Pt-DLN films. The changes observed in the annealed Pt-DLN films are very similar to that obtained by Dillon et al. for annealing studies on DLC films prepared by means of rf plasma deposition and ion beam sputtering [12].

DISCUSSION

With regard to the effects of annealing on the Pt-DLN films, following [12] we suggest that the increase in the I_D/I_G ratio with the simultaneous decrease in D and G linewidths is consistent with the removal of bond-angle disorder and the increasing dominance of the crystallites. The upward shift of the D and G peak positions indicates that the crystallites

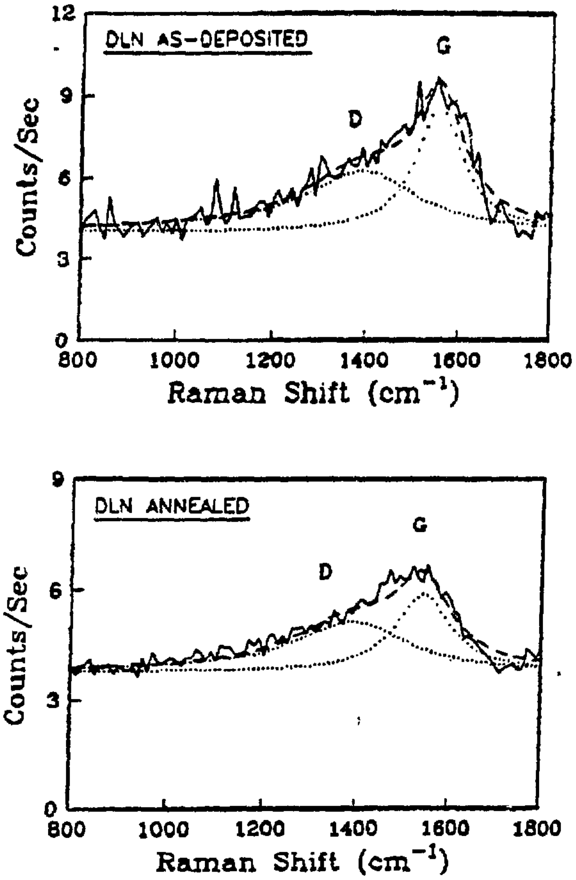

Fig. 3 Raman spectra at 300K of (a) as-grown and (b) annealed DLN films.

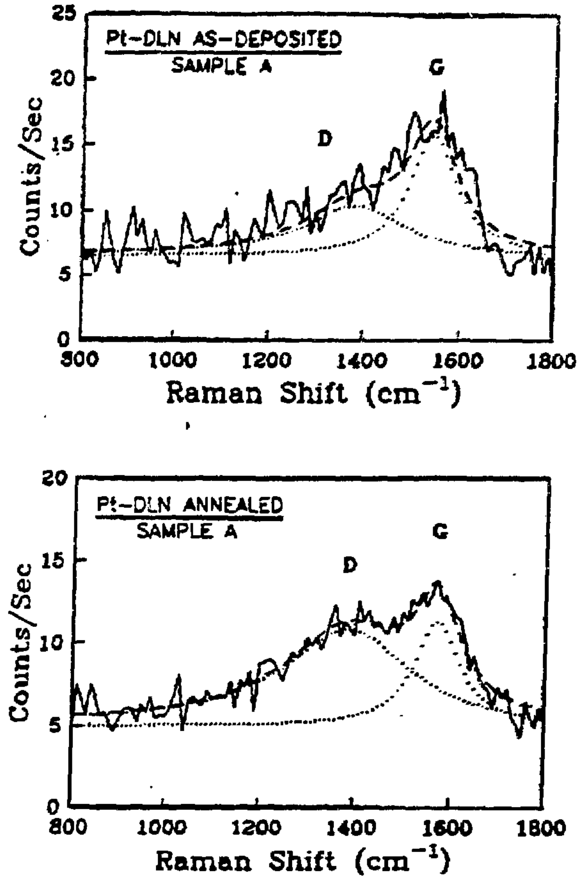

Fig. 4 Raman spectra at 300K of (a) as-grown and (b) annealed Pt-DLN (sample A) films.

Table I. Parameters of the Raman spectra of the different films.

Film type	I_D/I_G	ω_D (cm^{-1})	ω_G (cm^{-1})	$\Delta\omega_D$ (cm^{-1})	$\Delta\omega_G$ (cm^{-1})
DLN, as-deposited	1.17	1406	1556	304	126
DLN, annealed	1.28	1405	1542	289	144
Pt-DLN (sample A), as-deposited	0.87	1395	1543	251	121
Pt-DLN (sample A), annealed	2.53	1404	1572	314	114
Pt-DLN (sample B), as-deposited	1.28	1423	1536	347	150
Pt-DLN (sample B), annealed	1.96	1402	1565	235	107

formed during annealing are threefold coordinated. The increase in Pt concentration promotes a "loosening" of the diamond-like matrix and enhances graphitization. The data are consistent with an increase in the sp^2 bonding fraction with an upward shift of the G peak established by means of electron energy loss spectroscopy [13].

Our STM investigation shows that the influence of annealing on Pt-DLN films is to change the surface morphology from structureless (see Fig. 5) to a recognizable graphitic pattern (see Fig. 6). This study represents a real-space measurement of these changes (for details see [15]). The relatively smooth surfaces in Fig. 5 indicate that the surface conductivity of as-deposited films is uniform. The STM image of annealed sample A, on the same scale as Fig. 5, shows surfaces separated into regions of higher and lower conductivity. When focusing onto conductive regions, the well known structure of aromatic graphitic rings can be unmistakably identified, as displayed in Fig. 6. This observation is consistent with the difference seen in the Raman spectra of annealed Pt-DLN films (see Table I). The STM images of sample B with less Pt doping showed only chain like orders with periodicity closed to graphite lattice spacing [15].

Both FTIR and Raman spectroscopy in the present paper, as well as other experimental techniques [16], did not reveal any Si-C bonding. The steric constraints induced by the phenil rings in the polyphenilmetilsiloxane probably destabilize the Si-C bonds as in [17] and decomposition occurs via cleavage of Si-C bonds (in our case in DC plasma discharge). When the principles of DLN synthesis are observed [6] carbon and silicon form separate networks. We assume that DLN is comprised of two networks: carbon "diamond-like" mainly in the form of sp^3 bonds, and a silicon "glass-like" network, resulting in a purely amorphous structure. The mutual stabilization of these interpenetrating atomic-scale filaments and the common random network structure prevent the structural transformation and growth of graphite carbon at high temperature. The introduced hard melting transition metals of the IV-VI groups of the periodic chart form a stable metallic network with some strong cross-linking Me-C bonding. It was found that graphitization did not occur in W-DLN films even after annealing at 1250°C [7]. Data from spectroscopic and STM studies of DLN and Cr-DLN films show another clear example of high thermal stability of properly designed atomic-scale composites. However, introduction of the noble metals such as Pt decreases film stability probably by lowering the energy barrier of diffusion processes.

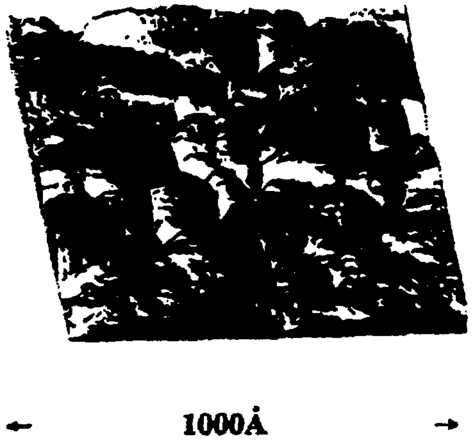

Fig. 5 STM image of an as-grown Pt-DLN film (sample A). Total z-variation ≈ 25 Å.

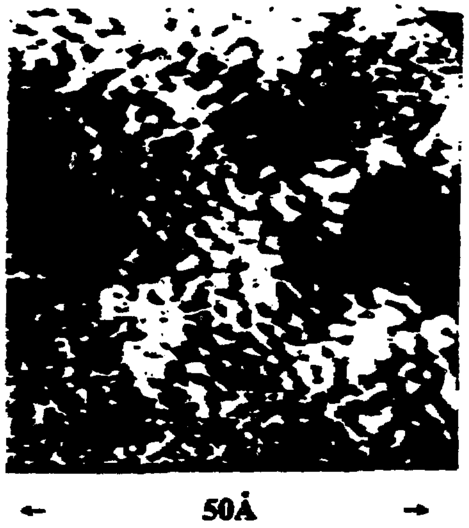

Fig. 6 STM image of an annealed Pt-DLN film (sample A). Total z-variation ≈ 5 Å.

CONCLUSIONS

We have performed a spectroscopic (Raman and FTIR) and STM study of atomic-scale nanocomposite films. It was shown that pure DLN and Cr-DLN films possess high thermal stability. Thermal annealing of Pt-DLN films produced an increase in the ratio I_D/I_G, a blue shift of D and G line positions and a decrease in the peak widths. This has been interpreted as a transformation from an amorphous structure with bond-angle disorder to that containing sp^2 carbon clusters. An increase in Pt concentration enhances this structural transformation. The graphite structure of the clusters was confirmed by STM.

ACKNOWLEDGEMENTS

The authors FHP and DY acknowledge the support of the NY State Science and Technology Foundation through its Centers for Advanced Technology program. and support provided by the U.S. Dept. of Energy, Div. of Materials Sciences under Contract No. DE-AC02-76CH00016

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