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A COMPARATIVE STUDY OF RESIDUAL STRESSES AND MICROSTRUCTURE IN a-tC FILMS

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ABSTRACT

We compare the microstructure of highly tetrahedrally-coordinated-amorphous carbon (a-tC) films prepared by pulsed laser deposition (PLD), measured using both small angle x-ray scattering (SAXS) and x-ray reflectivity, with other physical properties such as film stress and electrical resistivity. These properties are controlled by the film growth conditions and film thicknesses. Films prepared under vacuum conditions exhibit a shift in the measured mass density, as a function of laser energy density. The density for films approximately 600Å thick approach that of crystalline diamond. The measured densities for thicker, approximately 1000Å films, exhibit a smaller shift, and a lower density value. This shift correlates to observed changes in film stress and electrical resistivity. The small angle signal of the reflectivity spectra suggests the presence of layering, or in-plane density variations or a combination of both within the films.

INTRODUCTION

Amorphous highly tetrahedrally coordinated carbon (a-tC) films have potential in a variety of applications, from hard coatings to microelectronics. Therefore it is important to understand their structural, mechanical and electrical properties and how these relate to the method of film processing. These films consist of a mixture of carbon - carbon sp^2 and sp^3 bonds, grown in the absence of hydrogen. Previously reported results on a-tC films indicate the percentage of sp^3 bonds varies in the range of 77 - 90% sp^3 content [1,2]. In this study, pulsed laser deposition (PLD) is used to ablate carbon from a solid graphite target onto a silicon substrate at room temperature. The relative sp^2: sp^3 bonding ratio can be controlled depending on the growth conditions used, such as the laser wavelength, the laser energy density impinging upon the graphite target, or the background gas ambient during deposition [3,4].

Film properties obtained using Raman spectroscopy, as well as film stress [3] and electrical resistivity measurements [5], correlate with growth conditions in a manner consistent with the expected trend of sp^2: sp^3 bonding ratio. In general, film stress and electrical resistivity increase as the sp^3 content in the films increases. The films grown as described above are under high compressive stress, which varies from 1 to 6GPa as a function of increasing laser energy density. The stress is released when the films are grown in the presence of a background gas ambient [4]. Correlations made using Raman spectroscopy suggest that the effect of the gas ambient is to lower the kinetic energy of the ablated carbon species enroute to the substrate through collisional cooling.

In this paper, we present preliminary results of a reflectivity x-ray and small angle x-ray diffraction experiment on a-tC carbon films prepared using PLD in a high vacuum environment. We correlate results obtained on the density of the films with the measured stress in the films as

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well as to electrical resistivity measurements. The measured densities provide information that correlates with the sp^2:sp^3 ratio in the films. However, a precise measurement of this ratio is difficult due to lack of information on the densities of amorphous graphite and diamond.

EXPERIMENTAL

The a-tC films used in our study are grown by PLD, using 248nm pulsed laser radiation. A pyrolitic graphite target serves as the carbon source. The films are deposited on a rotating p-type Si (100) wafer. Details of the deposition process have been presented elsewhere [3]. The laser energy density varies between 10 and 45 J/cm^2, and the deposition rate is approximately 1Å/sec. Approximately 1/3 - 1/2 of the silicon wafer in each sample used in this experiment is left exposed. This enables the measurement and subtraction of a background scattering signal.

The stress in the films is obtained by measuring the curvature of the wafers before and after deposition, using a stylus profilometer [3]. The residual stresses are calculated using:

$$\sigma_f = \frac{E_s t_s^2}{6(1-\nu)t_f R}, \tag{1}$$

where E_s is the Young's modulus for the substrate, ν is Poisson's ratio for the substrate, t_f and t_s are, respectively, the film and substrate thickness and R is the radius of curvature [4].

X-ray reflectivity has been used to characterize amorphous carbon films with thicknesses ranging between 200Å and 1100Å [6-8]. This technique is useful in the determination of film thickness, roughness, and density. The thickness of the films can be determined by the oscillations in the reflectivity signal. The film roughness can be determined by measuring the exponential decay of the signal. The density of the films was obtained from the reflectivity measurements using:

$$\phi_c^2 = 2 * N_o (e^2/2\pi mc^2)(Z\rho/A)\lambda^2, \tag{2}$$

where ϕ_c is the critical angle, N_o is Avogadro's number, Z is the average atomic number, A is the average atomic mass, ρ is the mass density of the sample, and λ is the x-ray wavelength [6,7,9].The analysis of the small angle diffraction signal gives information on the presence of layering or clustering due to density variations within the films[8]. Layering gives rise to modulations in the oscillations due to film thickness in thin films. The presence of clustering or density variations can give rise to excess scattering at small angles or peaks at small angles.

In this experiment, we have combined both x-ray reflectivity and small angle x-ray scattering to determine the structure of the a-tC films. These measurements have been performed at the National Synchrotron Light Source, beamline X22A, using 1.20373Å (10.3keV) x-rays. The experimental resolution, achieved with a Si(111) monochromator and Si(111) analyzer, is $\Delta E/E \approx 1 \times 10^{-4}$ FWHM.

RESULTS AND DISCUSSION

Several a-tC films prepared at different laser energy densities under vacuum have been studied using the x-ray techniques described above. We have measured the x-ray reflectivity spectrum on a series of samples 250Å, 600Å and 1000Å thick prepared at laser energy densities of 11J/cm^2, 27J/cm^2 and 45J/cm^2 respectively. Figure 1 shows the x-ray reflectivity spectrum of a 600Å thick film prepared under vacuum with a laser energy density of 11J/cm^2. Note that in addition to the periodic oscillations which are proportional to the film thickness, the spectrum

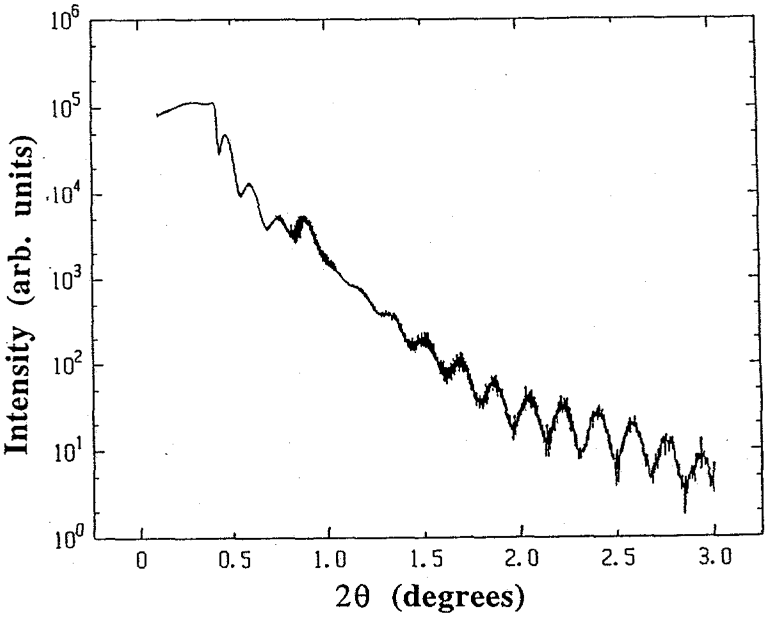

Figure 1. X-ray reflectivity curve for an at-C sample prepared at a laser energy density of 11J/cm^2 under vacuum. Note the extra scattering around 2θ = 0.8°.

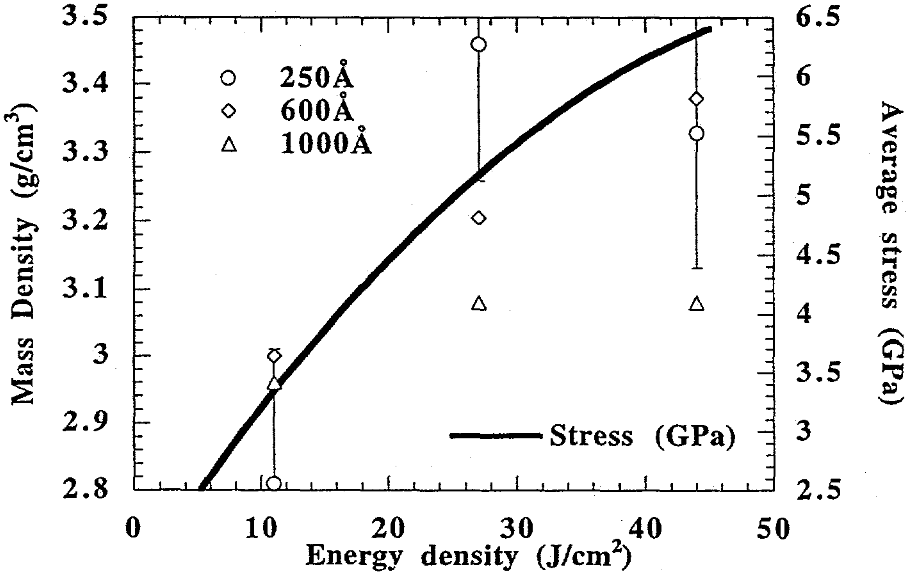

Figure 2. Mass density as a function of laser energy density for at-C films prepared in vacuum. The error bars in the measurements for the 600Å and 1000Å films are contained within the symbol. The solid line is the experimentally measured compressive stress curve (ref. 3). No fit has been performed for the mass density results as a function of stress.

shows excess scattering around $2\theta = 0.8°$, which may be related to density contrast between the film and substrate, at the film surface or to lateral density fluctuations within the film itself.

Figure 2 presents the results of a preliminary density measurement obtained from similar spectra of samples 250Å, 600Å and 1000Å thick. As a comparison, we plot the average compressive stress as a function of laser energy density [3,4]. As a function of film thickness, the mass density measurement shows a tendency toward higher values at medium and high laser energy densities. In previous studies [6], the measured densities were used to calculate roughly the percentage of sp^3 to sp^2 bonding in the film, using:

$$\rho = [\frac{(1-x)}{\rho_g} + \frac{x}{\rho_d}]^{-1}, \qquad (3)$$

where x is the sp^3 bond fraction, and ρ_g and ρ_d are the mass densities of crystalline graphite and crystalline diamond, which are $2.25 g/cm^3$ and $3.51 g/cm^3$ respectively. Using equation 3, the sp^3 bond percentage varies from approximately 77% to over 90% in the 600Å and 1000Å thick films studied. However, we note that amorphous graphite samples are typically less dense than crystalline graphite, with reported densities as low as $1.8 g/cm^3$. It is likely that pure amorphous diamond would also be less dense than crystalline diamond; recent molecular dynamics calculations suggest the most stable amorphous sp^3 bonded carbon material has as density of approximately $3 g/cm^3$ [11]. For this reason, it is difficult to calculate the precise sp^2:sp^3 ratio based on a linear interpolation of density using the values for both graphite and diamond, such as equation 3. However, since the density associated with sp^3 bonding is higher than that associated with sp^2 bonding, any increase in film density may be correlated with an increase in sp^3 bond content.

The functional shape as well as the position of any excess small angle scattering peaks, if present, give information on the density fluctuations within the samples. The angular position of any peaks present is proportional to a characteristic length or size of the density fluctuation. Figure 3 shows the preliminary results for the positions of the excess scattering peaks as a function of laser energy density for the 600Å and 1000Å samples respectively. These are expressed in terms of angstroms.

We now discuss the results presented above. A higher concentration of tetrahedrally coordinated carbon atoms should result in a higher compressive stress in the films and an increase in electrical resistivity. The trends observed in the average mass density of a-tC films prepared under vacuum as a function of laser energy density correlates with changes in the sp^2:sp^3 ratio inferred from Raman measurements as well as with the stress and electrical resistivity measurements [3-5].

The distribution of sp^2 and sp^3 bonded regions within the films will affect the residual stress of the films as well as the electro-optical properties of the film. As mentioned above, the intensity of the reflectivity signal as well as the presence and location of extra scattering at small angles are related to the density contrast between the film and substrate as well as to density fluctuations in different regions within the film. Figure 3 indicates that the basic length scale of such fluctuations is in the order of 100Å. These density variations may arise as a result of internal layering within the films which give rise to graphitic or low density layers at the substrate-film interface [6,7] and at the air-film interface [6,10,12]. Similarly, these variations can be a result of a distribution of alternating sp^2 and sp^3 regions in the plane of the film, which we discuss below.

Previous measurements on amorphous carbon (aC) films prepared using other methods [6,7] indicate evidence of both a contamination layer at the air-film interface [7] as well as a thin low density interfacial layer at the film-substrate boundary [6]. The results of electrical measurements on a-tC samples presented elsewhere [5] seem to indicate the existence of conductive paths or shorts through the thickness of the samples, which are consistent with regions with a higher sp^2 content than the sample average. The density difference between these regions and the bulk of the films results in a scattering signal that depends on the average of the shape, size, and the number of these regions within the sample. Regions with a characteristic size in the order of tens to hundreds of angstroms scatter X-rays at low angles, as seen in Figure 1. In addition, the presence and number of such low density regions should result in a relief of the residual stress within the film. No such measurements are available at present. A more detailed analysis of our results which will give a better picture of the internal structure of the films is in progress. This analysis will benefit from localized bond-sensitive measurements, such as high-resolution EELS, as well as from glancing x-ray scattering measurements [13].

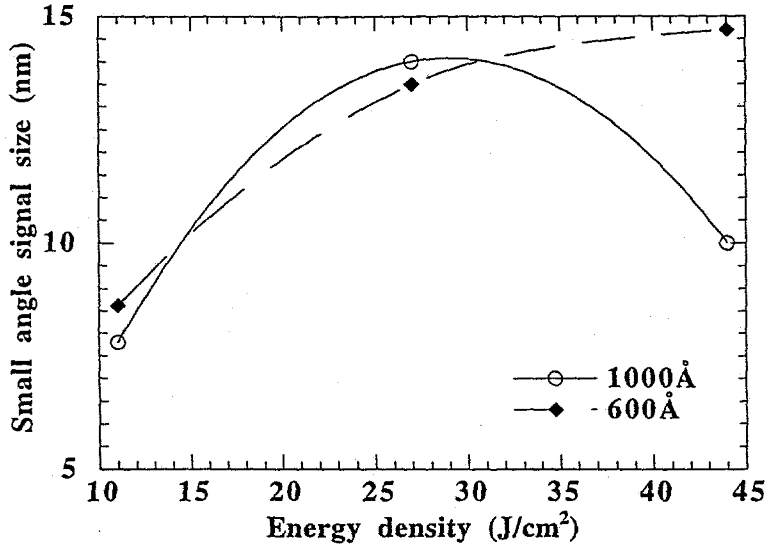

Figure 3. Small angle signal as a function of laser energy density for 1000Å and 600Å thick films prepared under vacuum.

Table I summarizes the measurements done on the 600Å and 1000Å thick films.

CONCLUSIONS

We have presented the preliminary results of an x-ray reflectivity measurement on at-C films prepared using PLD methods in vacuum. These results have been correlated to the residual stresses in the films as well as the measured electrical resistivities. For these films, the concentration of sp^3 bonds in the film, inferred from the preliminary mass density measurements correlate well with the results of the residual stress in the films as a function of laser energy density. Preliminary comparison of the reflectivity results with the resistivity measurements suggest that the films may contain in-plane density variations, as well as layering.

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Table I. Physical properties of a-tC films grown using PLD in vacuum, measured with SAXS and x-ray reflectivity.

Sample Thickness (Å)	Laser Energy Density (J/cm^2)	Average Film Density (g/cm^3)	Small angle signal (Å)
600	11	3.00	86 ± 6
	27	3.20	135 ± 6
	44	3.38	147 ± 6
1000	11	2.96	78 ± 10
	27	3.08	140 ± 10
	44	3.08	100 ± 10

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