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Characterization of Carbon Nitride Films Produced by Pulsed Laser Deposition

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ABSTRACT

Carbon Nitride (CN_x) films have been grown by ion-assisted pulsed-laser deposition (IAPLD). Graphite targets were laser ablated while bombarding the substrate with ions from a broad-beam Kaufman-type ion source. The ion voltage, current density, substrate temperature, and feed gas composition (N_2 in Ar) have been varied. The resultant films were characterized by Raman, Fourier transform infrared (FTIR), and Rutherford back scattering (RBS) spectroscopy.

Samples with ~30% N/C ratio have been fabricated. The corresponding Raman and FTIR spectra indicate that nitrogen is incorporated into the samples by insertion into sp^2-bonded structures. A low level of $C\equiv N$ triple bonds is also found. As the ion current and voltage are increased with a pure Ar ion beam, Raman peaks associated with nanocrystalline graphite appear in the spectra. Adding low levels of nitrogen to the ion beam first reduces the Raman intensity in the vicinity of the graphite disorder peak without adding detectable amounts of nitrogen to the films (as measured by RBS). At higher nitrogen levels in the ion beam, significant amounts of nitrogen are incorporated into the samples, and the magnitude of the "disorder" peak increases. By increasing the temperature of the substrate during deposition, the broad peak due mainly to sp^2-bonded C-N in the FTIR spectra is shifted to lower wavenumber. This could be interpreted as evidence of single-bonded C-N; however, it is more likely that the character of the sp^2 bonding is changing.

INTRODUCTION

Recently, much experimental activity has been directed towards attempts to synthesize the carbon nitride compound (C_3N_4) of β-Si_3N_4 structure theoretically predicted by Liu and Cohen[1]. This compound is predicted to have hardness properties near that of diamond.

Synthesis of this material either in bulk or thin film form has yet to be reported and confirmed by other investigators. Several groups have tried various techniques to synthesize this structure. Some of the attempted methods include ion-beam assisted deposition[2], reactive RF-magnetron sputtering[3, 4], electron cyclotron resonance plasma deposition[5], ion implantation into carbon films[6], e-beam evaporation of carbon with concurrent nitrogen ion bombardment[7], pulsed laser deposition (PLD) into a background gas of nitrogen[8, 9], PLD with an atomic nitrogen beam source[10], PLD with a radio frequency (RF) plasma assist[8], and ion-assisted PLD[11-13](IAPLD).

In general, the synthesis of hard tetrahedrally-bonded compounds that are usually only stably formed in the bulk at high temperature and pressure requires the use of energetic deposition techniques. For example, we have used PLD to synthesize amorphous-tetrahedral carbon (a-tC) films with a high sp^3-fraction[9, 13, 14], and also IAPLD to successfully form cubic-BN films[15]. Due to the success of PLD and IAPLD in growing similar materials, it is logical to expect this deposition technique to be a powerful tool for examining the formation and growth of CN_x materials. The motivation of this study is to controllably introduce nitrogen into a-tC films and examine the effect of ion bombardment on film structure and properties. We have deposited CN_x films under the concurrent bombardment of nitrogen and argon ions from a broad beam Kaufman-type ion source. The resultant films have been characterized by Fourier-transform infrared (FTIR), Rutherford back scattering (RBS), and Raman spectroscopies.

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EXPERIMENTAL

The PLD vacuum chamber is described elsewhere[13]. It is capable of attaining a base pressure of 1 x 10^{-6} Pa and is equipped with a broad-beam Kaufman-type ion source. The pyrolytic graphite targets (Union Carbide) were ablated with a KrF (248 nm) laser capable of generating 450-mJ pulses of 17-ns duration. The deposition time was 20 minutes at a laser repetition rate of 20 Hz. Samples grown at elevated temperatures were deposited at a 40-Hz repetition rate. The laser light was focused into the vacuum chamber using a spherical lens with a 35-cm focal length. The laser beam illuminates the rotating target at a 45° angle from the target normal. The beam forms a rectangular spot on the target with an area of 0.01 cm^2, giving an energy density of 45 J/cm^2. To improve the thickness uniformity, the sample substrate was rotated, the center of the ablated plume struck the substrate off the center line, and the sample substrate was 18 cm from the target. Using these conditions, we obtain an ablation deposition with ±10% thickness uniformity over 10-cm diameter wafers at an ablation deposition rate of 0.2 Å/pulse (no ion beam) for a total sample thickness of 1250 ± 250Å. Before deposition, the uncoated silicon (100) substrates (n-doped with P to 0.02 Ωcm) were cleaned to remove the surface oxide layer by a wet dip procedure in a HF/NH_4F solution[16]. The "room temperature" rotating Si substrates were not actively heated during deposition, although some residual heating (< 75 °C) occurred due to the power dissipated by the normal operation of the ion gun and condensation of energetic species from the ablation plume. Sample depositions at elevated temperature were performed by resistively heating the Si substrate. The temperature was measured by a bare thermocouple pressed directly to the back of the wafer.

The 3-cm Kaufman-type ion source (at a 10 cm separation from the substrate) was aimed (coincident with the laser plume) at a 25° angle from the substrate surface normal and slightly off axis from the center of the rotating Si substrate. The current density at the substrate was measured with a biased (-30V) retractable ball of 1 cm^2 diameter. For this study, the experimentally varied parameters were the ion feed gas composition (0 - 100% flow of N_2 in argon at a constant total flow of 4 sccm), the ion energy (0 - 1000 eV), and the ion current density (0 - 260 $\mu A/cm^2$). During deposition the background gas pressure in the chamber was ~2.7 x 10^{-2} Pa.

To measure the effect of the ion beam on the atomic bonding, the films were characterized by Raman spectroscopy (514 nm light at 50 mW of power) and FTIR spectroscopy. Graphite has two Raman active modes at 1350 cm^{-1} and 1581 cm^{-1}. The Raman band at 1580 - 1590 cm^{-1} (the "graphite" or "G" peak) is a fundamental Brilloun-zone-center mode of graphite. The Raman band at 1350 - 1360 cm^{-1} (the "disorder" or "D" peak) is believed to be a Brilloun-zone-edge phonon mode that intensifies for graphite crystal domains less than 100 nm in size. "Glassy" carbon is a nanocrystalline graphitic phase with broad Raman peaks near 1360 cm^{-1} ("D") and 1590 cm^{-1} ("G"). Raman bands due to sp^3-bonded carbon are obscured by strongly resonance enhanced signals from sp^2-bonded. The signal from sp^2-bonded carbon atoms tends to obscure any signal due to sp^3-bonded carbon atoms[17]. In FTIR spectroscopy, these symmetric modes are normally not present; however, the presence of nitrogen incorporated into "graphite-like" rings makes these modes IR active[18]. In addition, C≡N triple bonds appear near ~2190 cm^{-1}[19].

A parametric study was undertaken in order to understand the effects of varying ion beam deposition parameters. All the samples in this study were deposited using the same laser energy density (45 J/cm^2). The present paper focuses on the changes in the Raman and FTIR spectra as a function of varying ion beam deposition parameters.

DISCUSSION

Fig. 1a depicts FTIR spectra for samples grown with varying percentages of N_2 gas in Ar (V_b = 1000 V, I_b/A = 260 $\mu A/cm^2$). Also depicted in Fig. 1a is the nitrogen content of the samples as determined from RBS. The sample grown with a pure N_2 gas feed has a 28% N/C ratio. The nitrogen was distributed uniformly throughout the thickness of the film. As the nitrogen content of the samples increases, a broad peak in the FTIR appears centered near 1245 cm^{-1} that is partly due to nitrogen incorporation into sp^2-bonded structures[18]. It is possible that some of the intensity under this broad peak could be due to C-N single bonds of the type found in a $\beta-C_3N_4$ structure; however, it is not possible to make a more definite statement without other structural information

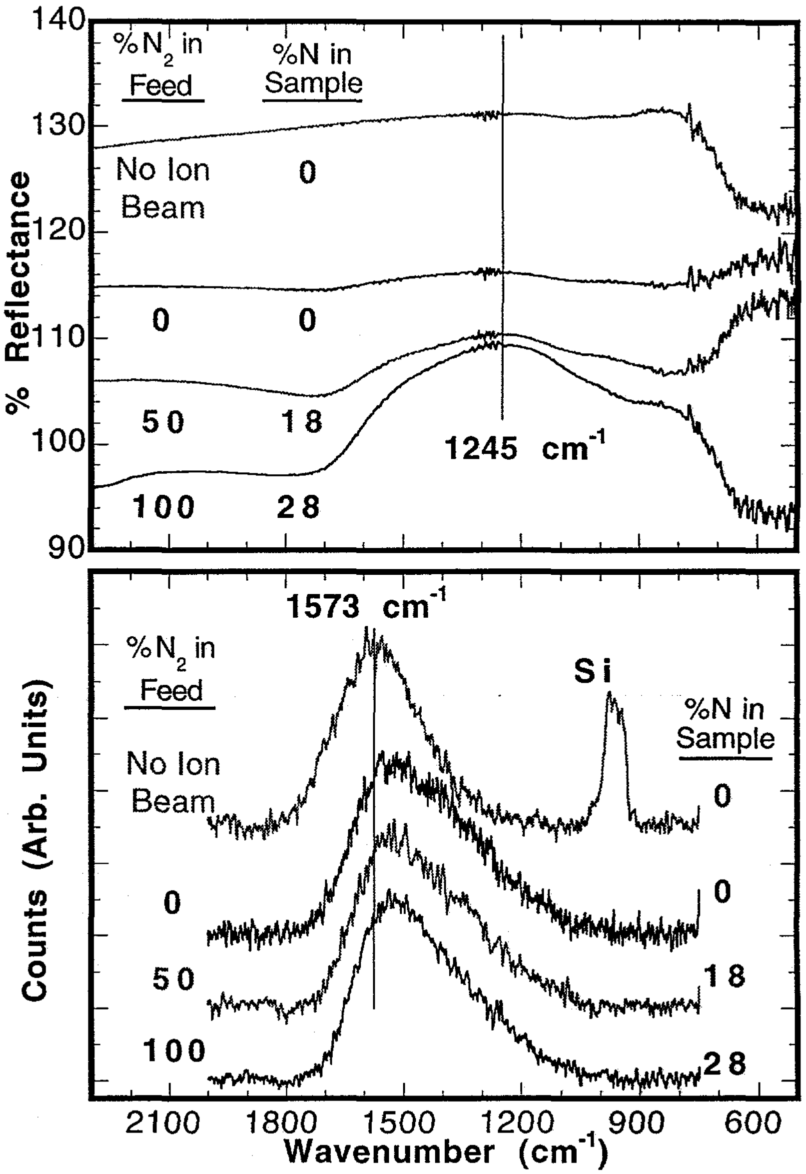

Fig. 1a) %FTIR reflectance for varying feed gas composition (N_2 in Ar) for I_b/A = 260 µA/cm^2 and V_b = 1000V. Fig. 1b) Raman intensity for the same samples in Fig 1a).

(e.g. electron diffraction) or knowledge of exactly where the peak should lie in the FTIR. A more likely possibility is that there exists a broad distribution of structures that are responsible for this peak (e.g. different size sp^2-bonded clusters of varying numbers of carbon and nitrogen atoms[20]). Variations in the nitrogen content of the samples results in different local bonding conditions producing changes in the FTIR peak shape and intensity. In addition, for the sample grown with 100% N_2 in the feed gas, there is an inflection point near ~2150 cm^{-1} that is evidence of C≡N triple bonding[19]. The FTIR spectra are featureless from 2300 - 4000 cm^{-1}.

Fig. 1b depicts the Raman spectra (normalized to constant height) of the same samples of Fig 1a. For reference, the sample grown with no ion beam shows a relatively symmetric peak centered at ~1570 cm^{-1} typical of a-tC films with a high sp^3 fraction[9, 14]. In addition, a second order Si substrate peak appears near 965 cm^{-1} whose intensity is an indication of the opacity of the carbon film samples. The sample grown with a pure Ar ion beam shows a much broader and asymmetric peak that has shoulders near 1590 and 1360 cm^{-1} suggesting that this sample has more graphitic carbon. In addition the film is more opaque as indicated by the disappearance of the Si Raman peak. It is clear that the ion beam is altering the a-tC structure causing significant graphitization. This is hardly surprising, given the relatively high ion energy used (1000 eV). Typically, most a-tC films grown by other techniques involve carbon ion energies from ~30-200 eV. At lower energies, sub-surface penetration of the ions does not occur resulting in graphitic samples; and at higher energies the films also become increasingly graphitic, possibly due to increased vacancy mobility[21]. For the samples grown with nitrogen in the ion beam (Fig. 1b), the Raman spectra are not significantly different, even for the sample containing 28% nitrogen. In combination with the FTIR spectra, this suggests that the a-tC structure is being broken down by high-energy nitrogen ion bombardment and that nitrogen is incorporated into sp^2 bonds with carbon.

In an attempt to reduce the graphitic content of the samples grown at high ion energies, a series of samples were grown at lower ion energy (V_b = 250 V) and current density (I_b = 80 µA/cm^2) and varying N_2 levels in the gas feed. The FTIR spectra and the nitrogen contents as determined from RBS from these samples are shown in Fig. 2a. In the FTIR spectra, there is little evidence of nitrogen incorporation till the feed gas is 100% N_2, where the measured nitrogen content is 18% and a broad peak appears in the FTIR centered near 1280 cm^{-1}. For ion feed gas compositions lower than 25% N_2, the nitrogen content was not detectable by RBS (the sensitivity in this measurement was ± 1%). The FTIR spectra in Fig 1a and Fig. 2a with similar nitrogen content (~18%) are similar in appearance suggesting the reduced ion voltage and current density do not seem to have affected the film structure.

Fig. 2b depicts Raman spectra (normalized to constant height) taken from the same films shown in Fig. 2a. The second order silicon peak is nearly absent for the samples grown in 100% N_2 and 100% Ar, but reappears for samples with a mixture of N_2 and argon. As discussed above, the intensity of this peak is a measure of the opacity of the samples. As has been suggested elsewhere, small amounts of nitrogen may help stabilize the sp^3 structure[4] of the material thus decreasing the film opacity. However, the Raman spectra from the sample with a high nitrogen content (18%) has shoulders near 1590 and 1360 cm^{-1}, indicating this sample is more graphitic.

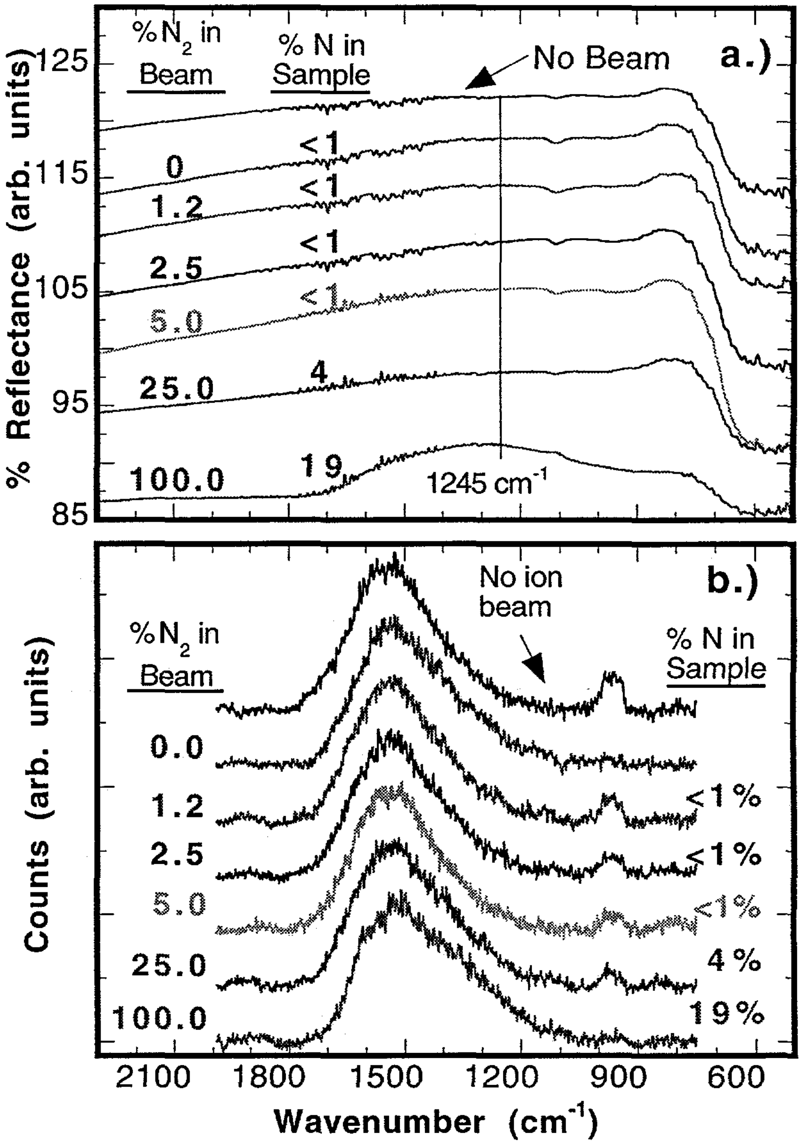

Fig. 2a %FTIR reflectance vs. wavenumber for varying feed gas composition (N_2 in Ar) for $I_b/A = 80\ \mu A/cm^2$ and $V_b = 250V$. (The dip at ~1105 cm^{-1} is due to SiO_2. The spectra are featureless from 2300 - 4000 cm^{-1}) Fig. 2b.) Raman intensity vs. for the same samples in Fig 2a).

The Raman spectra were fit to the sum of two gaussians centered near the positions of the G and D peaks of graphite to extract the ratio of their integrated intensities (I_D/I_G) as described elsewhere[13]. The results are plotted in Fig. 3 along with the RBS-determined nitrogen content of the films versus the percentage of N_2 in the feed gas. For low nitrogen content films, the ratio I_D/I_G shows a minimum near ~5% N_2 in the feed gas. This trend also correlates with the intensity of the second order Si peak and suggests that low levels of nitrogen may be beneficial in "healing" the a-tC network.

Amaratunga et al. have grown nitrogen-incorporated a-tC films by the filtered-cathodic arc method. It is interesting to note that they find low levels of nitrogen (≤1%) do not significantly alter the a-tC network and act as n-type dopants. At higher nitrogen contents (>1%) they find the a-tC network is significantly altered[22].) Fig. 3 suggests that the presence of low levels of nitrogen ions reduces changes to the a-tC network caused by the ion bombardment. As the amount of nitrogen in the structure increases the a-tC network again breaks down leading to the creation of a more graphite-like structure and increasing the opacity of the films.

(Naively, the higher the I_D/I_G ratio, the more graphitic the microstructure of the film.

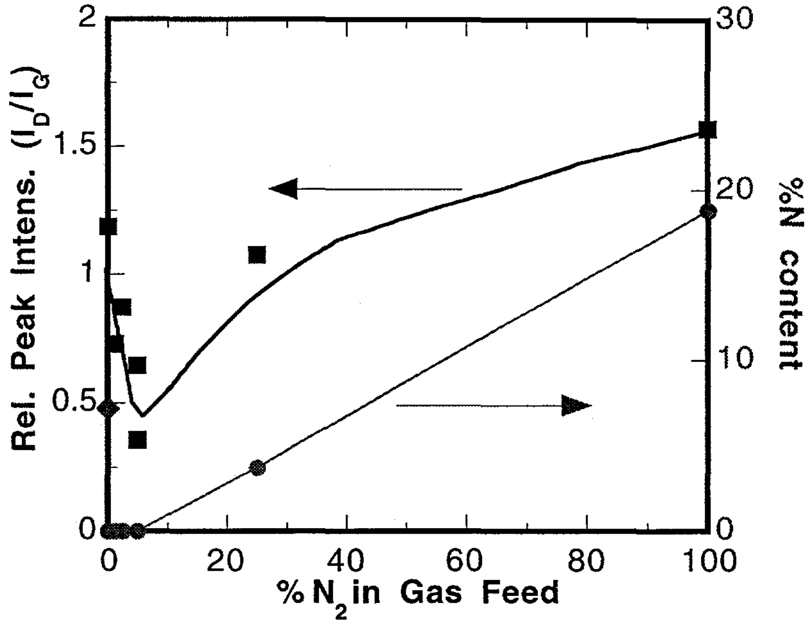

Fig. 3 I_D/I_G ratio and %N content (determined by RBS) versus $\%N_2$ in the ion gun gas feed for the samples in Fig 2. The lines are drawn as guides to the eye. The diamond symbol is for a sample grown with no ion beam.

However, the Raman spectra of a-tC and CN_x films are sufficiently different from that of amorphous-graphitic carbon that this interpretation is probably too simplistic. Doyle and Dennison[20] have proposed a model for the Raman spectra of graphitic amorphous carbon based on distributions of sp^2-bonded carbon rings with different sizes embedded in a two-dimensional continuous random network. Since the Raman signal is mainly from sp^2-bonded material even for a-tC films with a high percentage of sp^3 bonds, we speculate that a similar approach (modified to account for a more 3D structure) to fitting the a-tC Raman spectra may be applicable here. We speculate that it may be more fruitful to think of changes in the Raman and FTIR spectra as changes in the makeup and distribution of sp^2-bonded rings or clusters. Other methods of characterization must be used to probe the sp^3-bonded part of the amorphous network.)

The FTIR spectra of samples deposited at elevated substrate temperatures are shown in Fig. 4. As the deposition temperature rises, the small peak due to C≡N triple bonding disappears and the broad peak due to nitrogen incorporation shifts to lower wavenumber. Since, a-tC films cannot be grown at deposition temperatures above 200 °C[21], the changes in the FTIR spectra could be related to underlying changes in the a-tC structure with temperature. We note that this shift is in the direction expected for lower C-N bond order. Interestingly, the irradiated region of these films is qualitatively much harder. A diamond scribe will easily scratch the unirradiated portion of the films, and significantly more pressure must be applied to scratch the irradiated region. At this time, more structural information must be gathered to make a definitive statement as to the reason for this increase in hardness.

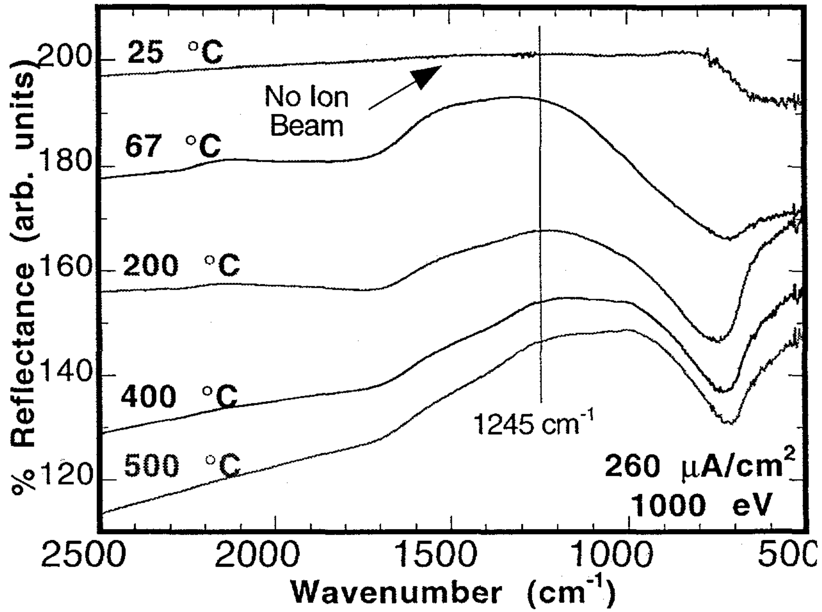

Fig. 4 FTIR intensity vs. for samples grown at varying temperature with $I_b/A = 300\ \mu A/cm^2$ and $V_b = 1000V$.

CONCLUSIONS

CN_x samples with $0 \leq C/N \leq 0.30$ have been grown using IAPLD. Effects of the addition of nitrogen to the samples can be seen in the FTIR and Raman spectra. The FTIR spectra show low levels of C≡N triple bonds and a broad peak centered near 1245

cm^{-1} that is due to nitrogen incorporated into sp^2 CN bonds. These FTIR peaks appear only in samples that have significant levels of incorporated nitrogen (as determined by RBS). In general, the Raman spectra indicate that films grown under ion bombardment near room temperature become more opaque and graphite-like. However, low levels of nitrogen incorporation (<1%) reduce the I_D/I_G ratio and decrease the opacity for the samples grown at 250 eV ion energies indicating a possible stabilization of the a-tC structure by nitrogen. Samples deposited at elevated temperatures show no evidence of C≡N triple bonds and an FTIR peak that shifts to lower wavenumber as the substrate temperature rises.

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