

Low temperature annealing in tetrahedral amorphous carbon thin films observed by ^{13}C NMR spectroscopy

Todd M. Alam,¹ T. A. Friedmann,² Peter A. Schultz,³ and Daniel Sebastiani⁴

¹*Department of Organic Materials, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

²*Department of Nanostructure and Semiconductor Physics, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

³*Department of Computational Materials and Molecular Biology, Sandia National Laboratories, Albuquerque, New Mexico 87185, USA*

⁴*Max-Planck Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany*

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For the first time to our knowledge, the ^{13}C solid-state magic angle spinning (MAS) NMR spectrum of a 99% ^{13}C enriched tetrahedral amorphous-carbon (ta-C) thin film containing a high concentration of fourfold coordinated carbon species (82%) is reported along with measured NMR spectra for the ta-C film after low temperature annealing (650 °C). Differential changes are observed for the ^{13}C MAS NMR chemical shifts and linewidths of both the fourfold (diamondlike) and threefold (graphitelike) coordinated carbon species within the thin films with increasing annealing time; however, there was no change ($\pm 2\%$) in the relative fourfold content. These spectral changes are associated with the large compressive stress reduction (6–8 GPa) in the carbon film. *Ab initio* calculations of the ^{13}C NMR chemical shift, along with shift variations as a function of atomic volume are reported for amorphous carbon and crystalline diamond. Using the observed spectral variations in the solid-state ^{13}C MAS NMR, along with the *ab initio* chemical shift calculations, the effect of annealing on the ta-C films is discussed and related to current models of thermal stress relaxation in ta-C thin films.

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I. INTRODUCTION

Tetrahedral amorphous diamond-like carbon (ta-C) thin films possess several desirable physical properties such as high hardness, low friction coefficient, ultra-wear resistance, chemical inertness, biocompatibility, and tunable electrical conductivity.^{1,2} Large growth stresses (6–12 GPa) have limited the applications of this material due to adhesion failure at the film substrate interface for relatively thin films ($\sim 0.1 \mu\text{m}$). It has been demonstrated that thermal annealing can completely remove the stress in ta-C thin films,^{1,2} and this fact has permitted the deposition of thick ($\sim 1\text{--}10 \mu\text{m}$) films.¹ It was also found that ta-C films could relax to slightly tensile conditions enabling the production of large free standing membranes.² Recently, micromachines built from stress-free ta-C films have been demonstrated.³

The nature of stress relaxation in ta-C thin films with annealing is still an open question. At least five different models have been proposed^{2,4–7} based largely on stress relieving bond transformations of the metastable structure. These transformations commonly involve a small percentage (1–9%) of the atoms in the structure and are difficult to quantify by standard characterization techniques. Transmission electron energy loss spectra are typically used to characterize the ratio of fourfold (diamondlike) to threefold (graphitelike) coordinated carbon. Recently ultraviolet Raman spectra have also been recorded that allow for a more quantitative interpretation of the relative bonding fraction. Under ideal conditions these experimental techniques are only sensitive to changes of $\pm 5\%$, and give no direct structural information such as changes in average bond length and bond angles, or the corresponding structural distributions. One technique that has been underutilized to this point is

solid-state ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. NMR has been applied to structural studies of threefold rich amorphous carbon,^{8,9} hydrogenated amorphous carbon,^{10–22} natural and synthetic diamonds^{23–28} and unique synthetically produced carbon materials,^{29–33} but only one NMR study has been reported for hydrogen-free ta-C films.⁹ In that study Golzan *et al.*⁹ used a sample collected from the carbon material that had delaminated from the fused silica growth substrate. This film delamination implies that any stress in the sample would be relieved before the NMR measurement. In addition, the ta-C film investigated by Golzan *et al.* had a lower relative concentration of fourfold coordinated carbon species (65%) than is reported in the current paper.

Recently we presented a solid-state ^{13}C MAS NMR investigation on the high temperature annealing effects in amorphous carbon thin films prepared using pulsed laser deposition and a highly enriched (99%) ^{13}C target.³⁴ The use of an enriched carbon source allowed the structural evolution of these thin films to be more readily followed using ^{13}C MAS NMR. In that study, a thick ta-C film ($\sim 6 \mu\text{m}$) was grown by repeated deposition, annealing (650 °C) and cooling cycles to provide a reasonably large sample size for increased signal to noise levels during the NMR investigations. The as-deposited film had a low fourfold coordinated carbon content (56%) as determined by ^{13}C MAS NMR. Further annealing of the amorphous carbon thin film between 800 and 900 °C, produced several distinct structural changes. The most notable change was the conversion of fourfold into threefold coordinated carbon species (87% threefold).

In this paper the first solid-state ^{13}C MAS NMR investigation of a high quality (82% fourfold coordinated carbon) as-deposited ta-C sample adhered to a Si substrate is re-

ported. Additionally, the ^{13}C MAS NMR spectra of the same film annealed for short times (1–4 min) at 650 °C were obtained to study the changes in the carbon environment during annealing. Theoretical calculations of the NMR spectra derived from calculated structures of amorphous carbon are also presented to quantify the structural changes that occur with annealing. The combination of theory and experiment allow an interpretation of these structural changes in light of possible stress relaxation mechanisms, along with a new understanding of thermal stress relief in ta-C thin films.

II. EXPERIMENTAL DETAILS

A. Thin film deposition

The ^{13}C enriched amorphous carbon films were prepared using approximately the same experimental procedure detailed previously.³⁴ Briefly, the carbon films were prepared by pulsed laser deposition (PLD) using an excimer laser (284-nm KrF) at high fluence ($>100\text{ J/cm}^2$) with a ^{13}C enriched graphite target in an ultra high vacuum capable vacuum chamber. First, an initial 100-Å natural abundance adhesion layer of carbon was deposited on both sides of a 100- μm -thick Si(100) wafer. To enhance adhesion to the substrate this natural abundance layer was annealed at 850 °C for 5 min. promoting carbide formation at the Si/C interface. A single, 0.35- μm -thick 99% ^{13}C -enriched carbon layer was then deposited on both sides of the silicon wafer. No additional thermal annealing was performed on the ^{13}C enriched layer prior to the NMR studies. The silicon wafers with the deposited carbon films were coarsely crushed and transferred to a MAS rotor for NMR analysis. Inspection of the resultant material revealed that the carbon film was still adhered to the Si substrate. Following the initial NMR studies, the sample was then annealed under flowing Ar gas at 650 °C using a rapid thermal annealing oven for 1-min intervals.

B. NMR measurements

The solid-state ^{13}C MAS NMR spectra were obtained on a Bruker AMX400 instrument at 100.1 MHz using a 4-mm broadband MAS probe spinning at 15 kHz. Direct polarization Bloch decay spectra utilizing 64-K scan averages and a 5-s recycle delay with no ^1H decoupling were obtained. Cross-polarization (CP) MAS NMR studies of these films showed no significant concentration of ^1H species in these films, as previously reported,³⁴ indicating that hydrogen plays no significant role in the stress relaxation process. Measured hydrogen contents of <2 ppm have been found in natural abundance ta-C films grown under similar conditions in our laboratory [D. Barnet (private communication)]. Saturation-recovery relaxation experiments were used to measure the spin-lattice relaxation time (T_1) for both the threefold and fourfold carbon species in these thin films which were found to be ~ 1 s. Experiments with long recycle delays (600 s) were also performed to assure that signal from carbon species having significantly longer spin-lattice relaxation were not being suppressed. For the results reported in this study, the sample size investigated corresponds to be-

tween ~ 0.5 and 1 mg of ^{13}C -enriched carbon. Under these conditions, all carbon atoms are probed by the NMR experiment with the exception of those associated with paramagnetic centers. Subsequent NMR measurements of the unannealed ta-C film at 100 °C revealed no temperature dependence of the chemical shift indicating negligible paramagnetic susceptibility. A two-dimensional exchange experiment, using a short 10- μs mixing time, was used to investigate the homogeneous linewidth. The details of this experiment have been previously discussed.³⁴

C. Theoretical structural calculations

To address the chemical shift variations in amorphous carbon, a series of 64-atom supercells at different volumes were generated, along with the calculation of the ^{13}C NMR chemical shift. The original 64-atom cell was taken from the 2.94-g/cm³ structure generated by Drabold, Fedders, and Stumm³⁵ (DFS) using molecular dynamics simulations with a minimal basis Harris functional method. This original cell contained 91% fourfold and 9% threefold coordinated carbon. This structure was then fully relaxed using a self-consistent local density approximation (LDA), Hamann norm-conserving pseudopotentials,³⁶ and a highly optimized Gaussian basis set in the QUEST program.^{37,38} The final equilibrated (Γ -point) structure contained 72% fourfold coordinated carbon, 28% threefold coordinated carbon, with a mass density of 3.10 g/cm³. A variation of the cell volume hydrostatically around this equilibrium volume allowed a sequence of supercells with different densities to be obtained.³⁷ Importantly, at each new volume, the atomic coordinates were allowed to relax to accommodate the volume change.

The ^{13}C chemical shifts of each individual carbon from the resulting relaxed amorphous carbon supercells at different volumes (and correspondingly different densities) were calculated using the NMR chemical shift module for extended periodic systems recently implemented³⁹ in the plane-wave based pseudopotential program package CPMD [computer code CPMD, <http://www.cpmid.org>]. These NMR calculations used the *ab initio* density functional theory (DFT) approach described by Sebastiani and Parrinello,³⁹ with the BLYP (Becke-Lee-Yang-Parr) exchange-correlation functional.^{40,41} A wave function cutoff of 60 Ry and pseudopotentials of the Goedecker type⁴² were used in calculations of the ^{13}C chemical shifts. The sampling of the Brillouin zone was restricted to the gamma point. The atomic coordinates from the QUEST LDA-relaxed cells were used in the analysis; an atomic relaxation of one of the cells at the DFT/BLYP level of theory was found to change the total energy of the system by less than 0.1 kJ/mol per carbon atom. The ^{13}C chemical shifts were referenced to that of crystalline diamond ($\delta = +39$ ppm) calculated under the same theoretical conditions as the amorphous systems above. For diamond, the variation of the chemical shift with volume was obtained by scaling the system's lattice constant and placing the carbon atoms at their ideal crystal lattice sites of a cubic 64-atom unit cell.

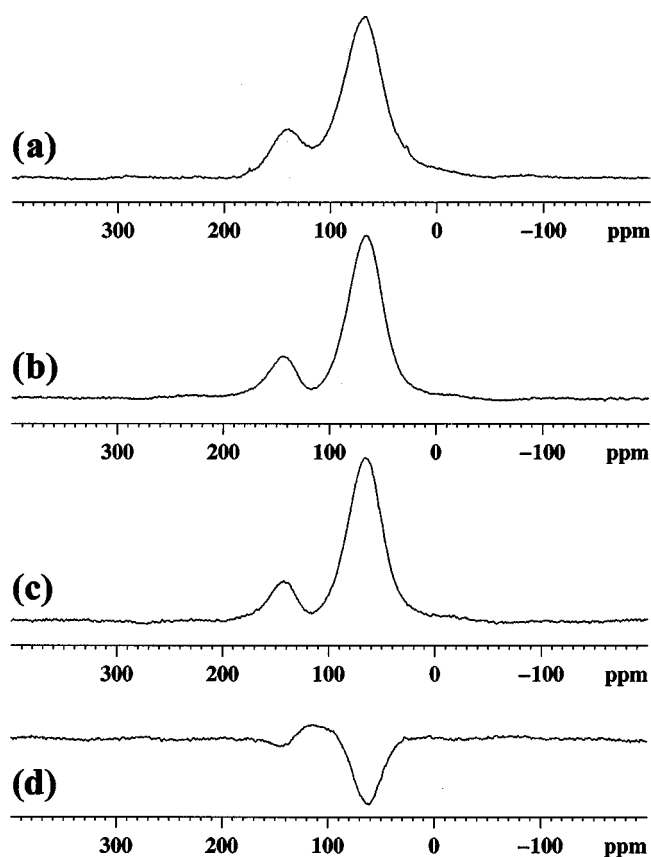


FIG. 1. The ^{13}C MAS NMR spectra of the ^{13}C enriched amorphous carbon thin films as a function of annealing time, (a) unannealed, (b) 2 min at 650°C and (c) 4 min at 650°C . The expanded ($2\times$) difference spectrum between the unannealed and the 4 min annealed spectra is shown in (d). During annealing small reductions in the linewidth, a decrease in the fourfold bonded carbon chemical shift, and an increase in the threefold bonded carbon chemical shift are observed.

III. RESULTS

A. Experimental NMR

1. ^{13}C MAS NMR of ta-C films

The solid state ^{13}C MAS NMR spectra of the ta-C film as a function of annealing time at 650°C are shown in Fig. 1. The isotropic chemical shifts (δ), full width at half maximum (FWHM) linewidths, and the relative fraction of the threefold coordinated ($\delta = +137$ to $+145$ ppm) and fourfold coordinated ($\delta = +64$ to $+69$ ppm) carbon species are tabulated in Table I. This ta-C film reveals a very high concentration of the fourfold (diamond-like or sp^3 -like) coordinated carbon species ($\sim 82\%$) as a result of the high laser fluence utilized during sample preparation. Importantly, there is no change in the fourfold content (within experimental error of $\pm 2\%$) for the short 650°C annealing times (Table I). With increasing annealing time there is a decrease of the fourfold carbon chemical shift and an increase in the chemical shift of the threefold carbon species. These changes in the chemical shift and linewidth are clearly visible in the difference spectrum [Fig. 1(d)] between the unannealed carbon

TABLE I. The ^{13}C MAS NMR isotropic chemical shifts, linewidths, and relative percent concentrations for amorphous carbon thin films as a function of low temperature annealing.

Sample ^a	δ (ppm) ^b	FWHM ^c (Hz)	f (%) ^d	Carbon species
Unannealed	69.1 ± 0.5	4657 ± 200	82	Fourfold
	137.8 ± 0.5	4563 ± 200	18	Threefold
1 min 650°C	66.5 ± 0.5	4054 ± 200	82	Fourfold
	145.9 ± 0.5	3679 ± 200	18	Threefold
2 min 650°C	64.9 ± 0.5	4103 ± 200	82	Fourfold
	143.6 ± 0.5	3189 ± 200	18	Threefold
2 min 650°C	65.0 ± 0.5	4083 ± 200	82	Fourfold
	139.4 ± 0.5	3287 ± 200	18	Threefold
3 min 650°C	65.3 ± 0.5	3987 ± 200	83	Fourfold
	143.8 ± 0.5	3182 ± 200	17	Threefold
4 min 650°C	66.0 ± 0.5	4013 ± 200	83	Fourfold
	143.3 ± 0.5	3395 ± 200	17	Threefold

^aSample preparation conditions listing the annealing times for 650°C annealing.

^bThe ^{13}C isotropic chemical shift referenced to the carbonyl resonance of the external secondary reference solid glycine ($\delta_{\text{iso}} = +176.0$ ppm with respect to TMS $\delta_{\text{iso}} = 0.0$ ppm).

^cLinewidth, full width at half maximum, (FWHM).

^dRelative percent fraction obtained from full MAS spectral deconvolution. Estimated error $\pm 2\%$.

^eThis sample was annealed directly for 2 min. at 650°C .

film and the film annealed for 4 min at 650°C . Comparison of the signal integration in the unannealed film [Fig. 1(a)] and the integration of the magnitude representation of the difference spectra [Fig. 1(d)] reveals that $>30\%$ of the carbon intensity observed in the ^{13}C MAS NMR spectra are impacted during the annealing process. This change corresponds to $>15\%$ of the carbons in the film since the integration of the magnitude spectra sums the effects of both negative and positive intensities variations from the difference spectra.

The linewidth (FWHM) of the fourfold and threefold coordinated carbon resonances as a function of annealing time is plotted in Fig. 2. The linewidth of both resonances narrows dramatically as the film is annealed with most of the change occurring in the first two minutes. The relative change in linewidth for the threefold resonance ($\sim 30\%$) is twice that of the fourfold resonance ($\sim 14\%$). It is important to note that because the same carbon thin film is analyzed sequentially at each annealing time, the chemical shift and linewidth changes are not the result of slight differences in initial film preparation conditions and thermal history, but are a direct result of the annealing process.

2. Exchange NMR—evidence for inhomogeneous broadening

The observation of very broad line widths in these amorphous carbon films needs to be addressed. It has generally been argued that the broad resonances observed in amorphous carbon films result from the distribution of local carbon environments.^{9,10,14,18,34} However, other sources of

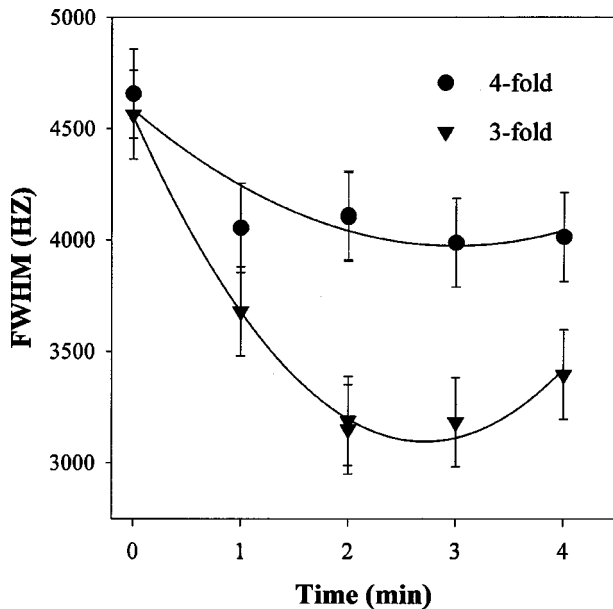


FIG. 2. Plot showing the experimental variations in the full width at half maximum (FWHM) linewidth for the fourfold and threefold coordinated carbon species in the amorphous carbon thin films with increasing annealing time (at 650 °C). The different carbon species show distinct differences in magnitude of narrowing with annealing.

broadening could contribute to the observed linewidths. For example, reported sources of broadening in diamond samples include paramagnetic²⁶ and dipolar²¹ contributions. In powder graphite samples³² broadening has been attributed to a large magnetic susceptibility anisotropy that could not be removed by MAS. We note that these reported contributions are small compared to the 4000–5000-Hz FWHM linewidths that have been reported for nonhydrogenated amorphous carbon films (Table I and Refs. 9 and 34).

To experimentally address the broadening question, a ¹³C two-dimensional (2D) exchange NMR experiment with a short 10- μ s mixing time was performed on the unannealed carbon thin film [Fig. 3(a)]. For this extremely short mixing time spin diffusion of the carbon magnetization between different carbon environments does not occur. This restriction of magnetization transfer produces a 2D exchange contour plot in which the carbon spectrum is projected along the diagonal, with no off-diagonal cross peaks observed except between the associated spinning sidebands. At longer mixing times, off-diagonal cross peaks resulting from magnetization exchange between different carbon environments were observed, and can be used to provide details on the local connectivity. These long mixing time 2D exchange NMR experiments will not be discussed here. The 2D projection of the ¹³C NMR spectra allows a method to measure the contributions from overlapping spectral components. Individual one-dimensional slices through the maximum of the fourfold resonance [Fig. 3(b)] and the threefold [Fig. 3(c)] coordinated carbon resonances allowed the measurement of the homogeneous linewidths of 250 and 270 Hz, respectively. These narrow homogeneous linewidths are significantly smaller than the 4657-Hz FWHM for the fourfold and the

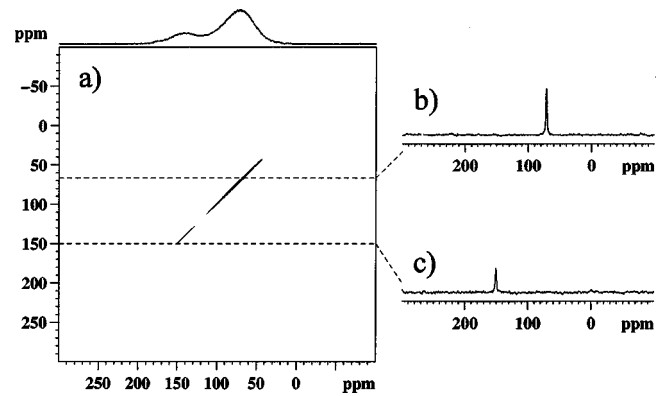


FIG. 3. Two-dimensional (2D) contour plot of the ¹³C exchange MAS NMR spectra (a) for the unannealed amorphous carbon film. Slices through the maximum of the (b) fourfold (diamondlike) coordinated carbon isotropic resonance, $\delta = +69.1$ ppm, and (c) the isotropic resonance of the threefold (graphitelike) coordinated carbon resonance, $\delta = +137.8$ ppm produce 1D spectra that reveal very narrow (~ 250 Hz) homogeneous linewidths. This experiment demonstrates that the broad 1D ¹³C MAS NMR spectra in Fig. 1 are inhomogeneously broadened, and represent distributions of local carbon environments.

4563-Hz FWHM for the threefold (Table I) coordinations obtained from the 1D ¹³C MAS NMR spectra [Fig. 1(a)]. The narrow homogeneous linewidths support the previous conclusion that the broad resonances observed in the 1D ¹³C MAS NMR result from distributions in the bonding environment of the carbon, and not from homogeneous paramagnetic or residual homonuclear dipolar broadening. This experimental observation thus allows variations in the ¹³C NMR linewidths and chemical shifts to be used as a measure of changes in the local carbon environment.

B. Theory

1. Comparison of theoretical and experimental ¹³C NMR spectra

Figure 4 shows a ¹³C NMR spectra obtained from a QUEST LDA-relaxed cell superimposed along with the experimental ¹³C MAS NMR spectra for the unannealed amorphous thin film of Fig. 1(a). A broad distribution in the chemical shift of the individual theoretical resonances was observed (bottom of Fig. 4). A line broadening of 300 Hz was added to the resonances of each individual carbon and summed to produce a spectrum, consistent with the experimental demonstration of inhomogeneous broadening (see section above) for the 1D ¹³C MAS NMR spectra. A direct comparison of the two spectra is complicated by the limited statistics (only 64 atoms) and the difference in fourfold coordinated carbon content of the theoretical (72%) and experimental (82%) samples. Bearing in mind these limitations, good agreement is found in that the simulated spectrum has two distinct spectral contributions made up of a broad distribution of overlapping individual resonances for the threefold and fourfold coordinated carbon atoms. The fourfold coordinated carbon resonance chemical shift ($\delta = +61$ ppm) is also in good agreement with experiment ($\delta = +69$ ppm), and significantly less shielded than the carbon in crystalline dia-

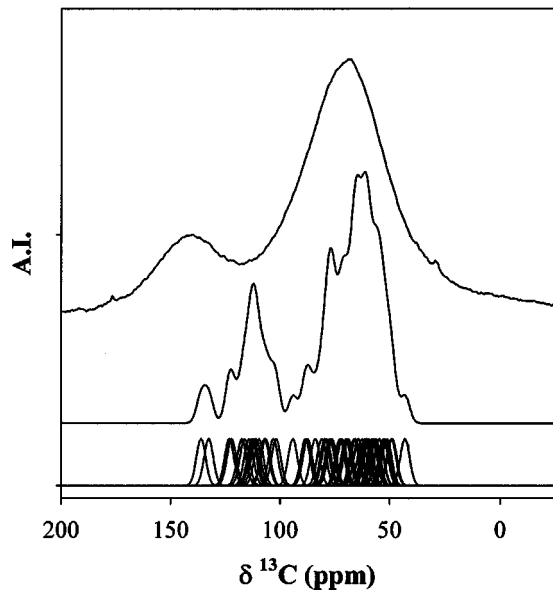


FIG. 4. Figure of the experimental ^{13}C MAS NMR spectrum for the unannealed carbon film (top), along with the *ab initio* ^{13}C NMR simulation for the amorphous carbon supercell (middle). The individual spectral component of each individual carbon within the simulated cell is also presented (bottom).

mond ($\delta = +36$ to $+39$ ppm). This result is similar to the $\delta = +75$ ppm maximum for the fourfold coordinated carbons reported previously by Mauri and co-workers for amorphous carbon.⁴³ These results support the earlier assignment arguments^{9,34} that amorphization of the diamondlike species produces an increase in the observed chemical shift similar to that observed in amorphous silicon.⁴⁴ For the threefold coordinated carbons the agreement between the theoretical peak maximum ($\delta \sim +110$ ppm) and experiment ($\delta = +138$ ppm) is not as good, and slightly smaller than that reported earlier ($\delta \sim +125$ ppm) by Mauri *et al.*⁴³ using a different ta-C supercell. The discrepancy between these two studies could result from either the different pseudopotentials or from the different ta-C supercells used in the ^{13}C NMR chemical shift calculations. Using the same supercell investigated by Mauri *et al.* (results not shown), we found very similar threefold and fourfold coordinated carbon peak positions, suggesting that the different results between the two theoretical studies are due to differences in the threefold carbon environments in the different super-cells used. Using either method for the *ab initio* NMR calculations (Mauri *et al.*⁴³ versus Sebastiani and Parrinello³⁹) results in an underestimate of the chemical shift separation between the threefold and fourfold carbon species when compared to experimental values. This difficulty in accurately predicting ^{13}C chemical shifts for different carbon species has been noted before. The chemical shift of the different carbon hybridizations are not quantitatively reproduced by simple constant corrections to the effective pseudopotential used in the calculations, and may result in errors on the order of 20 ppm.³⁹ While the absolute value of the ^{13}C NMR chemical shift obtained from these simulations may not correlate directly with experiment, it is felt that the relative trends and

variations in the chemical shift with structural changes, volume changes, or pressure changes are more reliable.

2. Calculation of chemical shift with volume and pressure variations

Instead of trying to correlate these chemical shift distributions with particular structural variation within the amorphous carbon, we found it more useful to determine the volume induced variations of the ^{13}C NMR chemical shift as used in previous studies.^{39,43} Figure 5(a) presents the predicted variations in the ^{13}C chemical shifts for crystalline diamond and the QUEST LDA-relaxed amorphous carbon structure as a function of atomic volume. For the amorphous carbon structure the variations of the *average* chemical shift for the fourfold coordinated carbons, the *average* chemical shift of the threefold coordinated carbons, along with the mole *averaged* chemical shift as a function of changes in volume are shown in Fig. 5(a). In all cases a linear relationship between changes in the *average* chemical shift and variations of the atomic volume ($d\delta/dV$) were observed. Crystalline diamond shows a $d\delta/dV$ variation of $+3.6$ ppm/a.u.³, very similar to the $d\delta/dV = 3.4$ ppm/a.u.³ value reported previously.³⁹ Since the same diamond structures were used in both of these calculations, this small ($\sim 5\%$) difference in the $d\delta/dV$ correlations for crystalline diamond results from the different plane wave cutoff levels utilized (60 versus 70 Ry). Differences in the effective core potential utilized in the NMR chemical shift calculations will have a negligible influence on the predicted slope of the chemical shift variation with volume. A much smaller $d\delta/dV$ variation is predicted from the amorphous carbon QUEST LDA-relaxed structures for both the fourfold and threefold coordinated carbons in comparison to the crystalline diamond. The *average* chemical shift of the fourfold coordinated carbon shows a $d\delta/dV = +2.5$ ppm/a.u.³ variation, while the *average* chemical shift of the threefold coordinated carbon shows a $d\delta/dV = +0.9$ ppm/a.u.³ variation. The mole-fraction weighted average variation of the ^{13}C chemical shift for the amorphous QUEST LDA-relaxed cell was $d\delta/dV = +2.0$ ppm/a.u.³, significantly smaller than the $d\delta/dV = +3.6$ ppm/a.u.³ variation observed for crystalline diamond.

The above correlations for the amorphous carbon QUEST-relaxed structure were determined using the variation of the *average chemical shift* with atomic volume. To address the question of chemical shifts versus volume variations for each *individual* carbon within the amorphous carbon structure Figure 5(b) shows a histogram of the chemical shift derivatives obtained for each carbon atom in the modeled supercell. The average of these individual $d\delta/dV$ variations is $d\delta/dV = +2.5$ ppm/a.u.³ ($\sigma = 0.6$ ppm/a.u.³) for the fourfold coordinated carbons and $d\delta/dV = +0.8$ ppm/a.u.³ ($\sigma = 0.6$ ppm/a.u.³) for the threefold coordinated carbon. The average values of the *individual* variations are very close to the variations observed for the *average chemical shift* variations discussed above, with the standard deviation providing an error bar for the $d\delta/dV$ variations. While the $d\delta/dV$ values are not defined by a normal distribution [Fig. 5(b)], there are clear differences between the fourfold and threefold coordinated carbons in the ta-C cell. Figure 5(b) also shows

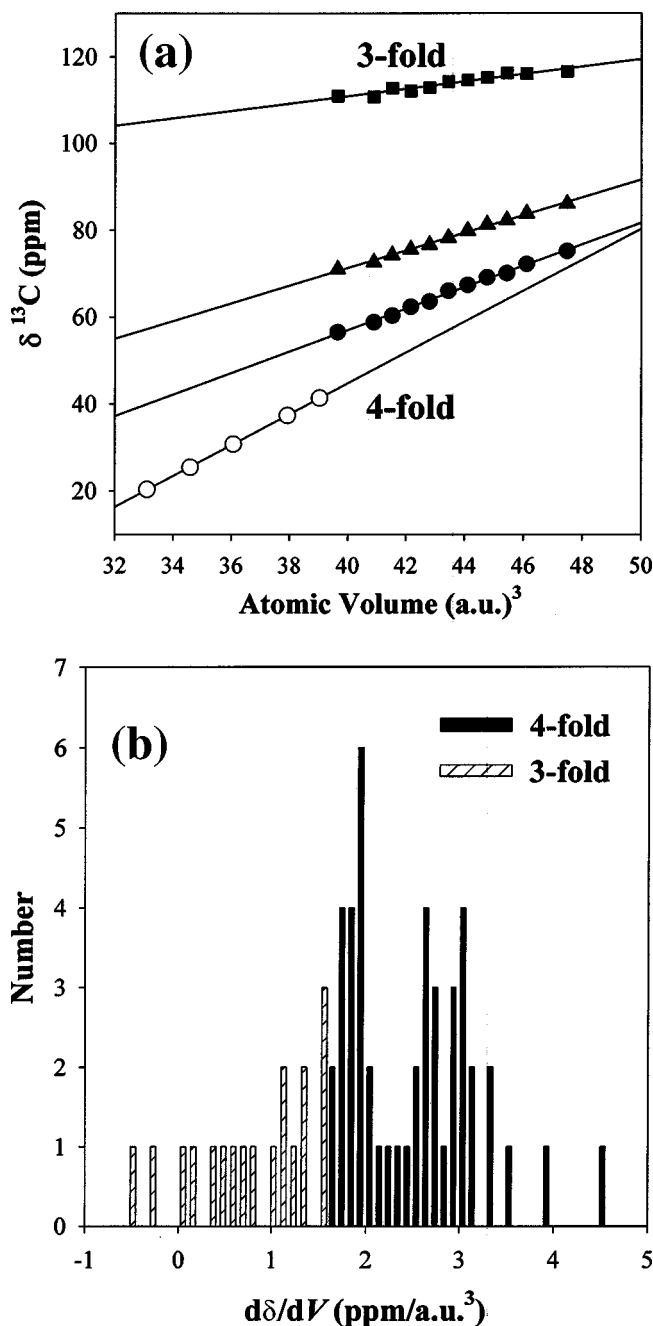


FIG. 5. *Ab initio* predictions of (a) the variation of the average ^{13}C chemical shift with increasing atomic volume for different systems, (○) crystalline diamond, (■) threefold coordinated carbon in the QUEST relaxed amorphous cell, (●) fourfold coordinated carbon in the QUEST relaxed amorphous carbon cell, and (▲) the mole fraction weighted average of the threefold and fourfold coordinated carbon chemical shifts in the amorphous cell. (b) The distribution of chemical shift vs the volume derivative ($d\delta/dV$) for the individual carbons in the QUEST relaxed amorphous cell.

that the $d\delta/dV$ variations for the fourfold coordinated carbon in amorphous carbon are significantly smaller than the $d\delta/dV = +3.6 \text{ ppm/a.u.}^3$ variation observed in crystalline diamond. These differences in the $d\delta/dV$ correlations demonstrate that the presence of different carbon connectivities within the structural network impacts the response of the

material to volume changes. These results also show that the ^{13}C NMR chemical shift behavior obtained from simulations of crystalline diamond is not directly transferable to amorphous carbon systems.

It is also possible to use these $d\delta/dV$ results to estimate the chemical shift variation as a function of pressure ($d\delta/dP$). Using the bulk modulus (B) of 445 GPa for crystalline diamond,⁴⁵ a $d\delta/dP$ variation of -0.29 , -0.20 , and -0.08 ppm/GPa is predicted for crystalline diamond, amorphous fourfold and threefold coordinated carbon, respectively. The crystalline diamond result corresponds nicely to the -0.30 ppm/GPa reported by Mauri *et al.* in their *ab initio* NMR calculations of crystalline diamond. With increasing pressure the atomic volume decreases, and correspondingly the ^{13}C NMR chemical shift will decrease (increased shielding) as reflected in the negative $d\delta/dP$ correlations. The value of $d\delta/dP$ calculated also depends on the value of the bulk modulus utilized. Using $B = 334 \text{ GPa}$ reported for amorphous ta-C films⁴⁵ containing 88% fourfold bonded carbons with a density of 3.26 g/cm^3 , the predicted $d\delta/dP$ correlations would be -0.27 and -0.11 ppm/GPa for the fourfold and threefold coordinated carbons in the QUEST relaxed amorphous cell.

C. Combining theory and NMR experiment

1. Correlation of chemical shift with fourfold bond length

Correlations between various structural parameters and the predicted ^{13}C NMR chemical shifts were also explored using these *ab initio* simulations. Attempts to observe correlations between predicted ^{13}C NMR chemical shift and average bond length or bond angles in the threefold carbon species were unsuccessful, most likely the result of the limited number of these carbon species in the simulated cell. In Fig. 6, an increase in the ^{13}C chemical shift with fourfold bond length ($\sim 187 \text{ ppm/\AA}$) was obtained for the simulated 3.10-g/cm^3 amorphous carbon cell. The increase in chemical shift with longer carbon-carbon bond distances is consistent with the decreased shielding caused by amorphization. The significant scatter observed in Fig. 6 suggests that in addition to simple bond length changes, variations of multiple structural parameters must account for the changes in the ^{13}C chemical shift. These structural variations may include changes in the carbon-bond angles and carbon-carbon bond distances, as well as the nearest bonded neighbor speciation. Nevertheless, this trend suggests that the narrowing of the NMR line shape with annealing results from modification of those bonds that are the furthest from the equilibrium crystalline length. The measured change in the average chemical shift of the fourfold bonded carbon with annealing is -4 ppm (Table I). This translates into an average bond length decrease of -0.021 \AA or -1.4% and a corresponding volume decrease of -4% . We note that this change is in the opposite direction that would be expected for relief of compressive stress.

2. Average local volume changes calculated from chemical shift variations

The species specific values for the $d\delta/dV$ variations obtained above, combined with the measured peak shifts (Table

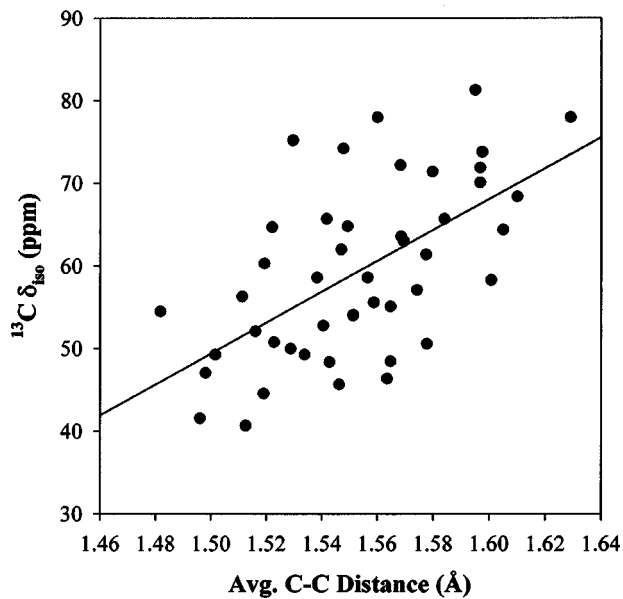


FIG. 6. Plot shows the variation of the predicted ^{13}C NMR chemical shift as a function of average carbon-carbon bond length for the fourfold carbon species in the relaxed amorphous carbon cell.

I) of the fourfold (-4 ppm) and threefold ($+6$ ppm) coordinated carbon, can be used to calculate the average local volume changes with annealing. We find that the fourfold coordinated carbon atoms give an average net volume *decrease* of $\Delta V/V = -4\%$, which agrees quite well with the volume decrease obtained from the variation of bond length in the previous section. The average threefold coordinated carbon volume *increases* with annealing and is even larger, $\Delta V/V = 13\%$. The net volume change of the structure using the mole-weighted average $d\delta/dV$ variation for a 82% fourfold coordinated carbon material is $< -0.3\%$. If the peak position shifts are solely a result of local volume changes, these changes imply a picture for the stress relaxation that is significantly different from our current understanding as will be described below.

Care must be taken in interpreting variations in the chemical shifts as other factors may contribute to the peak position. It is possible that the observed changes in the chemical shift may result from preferential relaxation of carbons with different connectivity. There is evidence from 2D radio frequency dipolar recoupling (RFDR) NMR experiments (Alam, unpublished results) that different ^{13}C chemical shifts exist for carbons with different next nearest neighbor connectivities. For example, the chemical shift of a fourfold coordinated carbon bonded to four other fourfold coordinated carbons is different from a fourfold coordinated carbon bound to two fourfold coordinated carbons and two threefold coordinated carbons. Resolution of these different carbon species is not obtained under simple 1D MAS NMR conditions, but instead these different carbon resonances overlap to produce the broad resonance seen in Fig. 1. It is conceivable that differential changes during annealing to the local environment for the different carbon connectivities (each with slightly different chemical shifts) could produce the ob-

served changes in overall average measured chemical shift. This is also consistent with Fig. 5(b), where the response of different carbons in the simulated supercell to changes in volume is highly varied. Future investigations using RFDR and multiple quantum NMR techniques may allow the spectral resolution of these differently coordinated carbon species to be achieved, but presently the extended range structure within the carbon network has not been determined using NMR.

3. Reduction of volume distribution (ordering) with annealing

The dominant change in the ^{13}C MAS NMR spectra with annealing is the reduction of the observed line width. It has previously been shown⁴³ for CVD grown crystalline diamond, through combined correlations of the variations in the ^{13}C NMR chemical shift and Raman linewidth, that the dominant source of broadening in both the NMR and Raman spectra are local fluctuations in the internal stresses (ΔP) or equivalently local fluctuations in the internal volumes (ΔV). For the ta-C films investigated here we have demonstrated that the ^{13}C NMR spectral lines are inhomogeneously broadened (Sec. III A 2) and therefore variations in this linewidth can be a measure of the changes in the local volume distribution. As noted previously there may be multiple contributions to the overall ^{13}C NMR linewidth, including distributions resulting from the next-nearest-neighbor speciation (i.e., how many threefold versus fourfold coordinated carbons is an individual carbon bonded to). Because of these different contributions, the total experimental line width will not be used as a direct measure of local volume distributions. Instead the change in the line width between annealed (quasi-equilibrium) and the unannealed (metastable) amorphous carbon film will be used to measure the change in the distribution of local atomic volume. From Fig. 2, the maximum observed reduction in FWHM for the fourfold coordinated carbon is ~ 680 Hz, with a larger reduction observed for the threefold coordinated carbon, ~ 1375 Hz (Table I). Using the $d\delta/dV$ variations obtained from the simulated changes of the average chemical shift with volume (Sec. III B 2), the observed line narrowing corresponds to a thermal reduction in the volume distribution of 2.7 and 15.3 a.u.³ for the fourfold and threefold coordinated carbons within the ta-C films. Note that this is not the change in the average volume, but the reduction in the atomic level volume distribution (or ordering) for the different carbon species. These ^{13}C NMR experimental results demonstrate that for these ta-C films changes in local volume distributions during annealing are inhomogeneous between the fourfold and threefold coordinated carbon. This differential response of the fourfold and threefold carbon species to annealing may play an important role in the stress reduction of films and the resulting materials.

IV. DISCUSSION

A. Models for stress relaxation in ta-C

Several different views on the origin of compressive stresses present in ta-C have been proposed^{5,46-48} (For a review see Lifshitz⁴⁹). The fact that these stresses can be annealed away without significant change in the fourfold con-

tent indicates that the stresses are not intrinsic to ta-C films, but are a consequence of the non-equilibrium growth process.⁶ In the as-deposited films metastable configurations are formed and retained due to the low growth temperatures <200 °C and medium ion energies (~100 eV). The structure then relaxes based on the thermal history. As an example, we have measured stress relaxation (~10%) in ta-C films stored at room temperature over a period of a year (Friedmann, unpublished results). These long-term low-temperature relaxations confirm the metastable nature of ta-C films. Several mechanisms for stress relaxation in ta-C thin films have been proposed. The NMR data can be interpreted in view of these different models as will be discussed below.

1. The Sullivan-Friedmann model (SFM)—stress induced fourfold to threefold conversion

The Sullivan-Friedmann model (SFM) of stress reduction is based on the conversion of fourfold coordinated carbons to threefold coordinated carbons.² By investigating the stress relaxation process as a function of time and temperature, they determined that the kinetics were that of a first order chemical reaction with a broad distribution of activation barriers extending from 0.5–3.0 eV. This experimental fact dictates that the stress relaxation is driven by strain relieving bond transformations in ta-C films. Since ta-C has a large Young's modulus (~800 GPa) only ~1% strain relief is necessary to fully relieve the compressive stresses typically observed in these films. The strain reduction in the SFM results from the shorter bond length of the threefold in-plane carbon-carbon distance (~1.42 Å) versus that of fourfold carbon (~1.54 Å) with the larger volume of the out-of-plane π orbital accommodated by preferential orientation parallel to the growth direction where the biaxially stressed film is free to expand. For full stress relief, this would require ~9% atomic conversion from fourfold to threefold carbon coordination.

2. Monteiro model—stress induced threefold to fourfold conversion

Monteiro *et al.*⁴ proposed an alternative model in which the stress reduction results from the opposite threefold to fourfold conversion. The mechanism for this conversion is that under high stress conditions the fourfold coordinated carbon configuration is more thermodynamically stable than the threefold bonding coordination. Thermal annealing provides the energy to promote this conversion. Once the stress is reduced below the thermodynamic limit favoring fourfold bonding, the SFM model would account for further stress reduction. For near complete stress relaxation, 1–3% conversion is required. This model was based on the observation that the ta-C film hardness and modulus actually increases slightly during annealing for filtered cathodic arc deposited films.

3. Siegal model—ordering

Siegal *et al.*⁷ also reported an increase in hardness with annealing on PLD grown films and a decrease in the film density (~7%). These films were examined by transmission

electron microscope bright field images that revealed contrast variations with annealing indicative of a nanoclustering into darker (dense) versus lighter (less dense) regions. The apparent ordering was proposed to be responsible for the increase in hardness, decrease in density and concurrent reduction in compressive stress.

4. Ferrari model—reorientation and clustering of threefold coordinated carbon

Ferrari and co-workers^{6,50} suggested that the stress reduction was due to a reordering of the threefold coordinated carbon phase with annealing from parallel to perpendicular with respect to the growth surface, as evidenced by Raman data that show clustering of the threefold coordinated carbon phase with annealing and electron energy loss spectroscopy (EELS) data that indicate a preferential orientation of the sp^2 π orbitals parallel to the growth substrate. Approximately 1% of the atoms in the structure would have to reorient in this manner to produce the required strain relief.

5. Kelires model—local atomic stresses

A model of local atomic level stresses has also been forwarded by Kelires and co-workers^{5,51–53} to explain the compressive stress in ta-C materials. The local stresses in this atomic level model arise due to disorder in amorphous materials produced by distributions in bond lengths and angles, along with structural incompatibilities. These structural incompatibilities include the inclusion of threefold carbons in environments rich in fourfold coordinated carbons, and vice versa. Using the atomic level stress model, simulations of ta-C have predicted that there is a wide distribution of local stress (± 100 GPa). It was found that the majority of the fourfold coordinated carbons (sp^3 -like) were under compressive stress, while the threefold coordinated carbons (sp^2 -like) were under higher average tensile stress. Interestingly, because the total volume of the simulated cells was allowed to vary, the simulations predicted that the total intrinsic stress was near zero, with the threefold carbon species relieving the internal compressive strain energy for systems containing mixtures of threefold and fourfold carbons. This relaxed cell should in principle be similar to the relaxed QUEST structure used above for the NMR calculations as the total volume was also allowed to relax. Stress reduction during annealing is expected to occur by removal of local structural incompatibilities, allowing the film to relax from the metastable state produced during film deposition to a quasi-equilibrium structure.

B. NMR interpretation of annealing

1. Changes in hybridization

The SFM (Refs. 2 and 4) involves the interconversion between fourfold (diamondlike) and threefold (graphitelike) coordinated carbon. It has been shown earlier by ¹³C MAS NMR that this conversion process readily occurs at higher temperatures.³⁴ For the ta-C films studied in the present investigation there is no significant change in the fourfold to threefold concentration (within the experimental error of

$\pm 2\%$) during the 650 °C annealing (Table I). This is well under the 8–9% conversion predicted by the SFM for complete stress reduction. Within the relative error of the line shape deconvolutions it is very possible that there is a small amount (1–2%) of interconversion between fourfold to threefold coordinated carbons (or vice versa), but clearly large changes in ratio of the carbon speciation are not produced by the annealing process.

The NMR data cannot rule out, or directly confirm, the Monteiro model since a smaller increase in the fourfold content ($\sim 1\%$) is needed to produce the required stress relief. It is doubtful that these subtle changes could be measured with Raman and/or EELS techniques. Perhaps with a larger sample size, and lower temperature annealing (to slow the kinetics) it may be possible to decrease the error in the NMR quantification allowing the observation of these subtle changes. Finally, the Ferrari and Kelires models are consistent with the lack of hybridization change.

2. Variations of the isotropic chemical shift

The +4.2 ppm (fourfold) and -6.0 ppm (threefold) change in the average chemical shift between the unannealed and the annealed film corresponds to an average decrease in the fourfold volume and increase in the threefold volume. When allowed to relax, the fourfold carbon atoms respond as if they are in tension reducing their average volume, while the threefold carbon atoms act as if they are in compression increasing their average volume. This aspect of the relaxation during annealing is not adequately captured by any of the current models. In particular, these changes are in the opposite direction one would expect from a straight-forward interpretation of the Kelires model.

3. Reduction of the NMR linewidth

The dominant change in the NMR spectra is the reduction in observed line width, especially that of the threefold carbon. An estimated $>15\%$ of the carbon atoms in the structure are affected by these rearrangements. This strongly supports the idea that the growth process is the source of stress and that ordering is the dominant relaxation mechanism. The inhomogeneous reduction in the volume distribution (ordering) during annealing for the fourfold and threefold coordinated carbon species is consistent with the ordering in both the Siegal and Ferrari models. The differential variation in local volumes also provides experimental evidence for the presence of differential response to local atomic stresses as proposed by Kelires.

C. What is the correct model?

The experimental observation that there is no net hybridization change indicates that the most likely model is one where bond rearrangement (e.g., angle, length, and orientation) is the source of stress relaxation. The NMR data show that both phases undergo reordering (line narrowing), so that models that rely only on threefold or only on fourfold ordering are probably not complete. When relaxing the original DFS structure we found that small changes in volume would produce a cascade of bond changes in the structure as local

metastable bonding environments responded to the perturbation. These rearrangements involved both phases and included net hybridization changes as well as bond angle and length changes. Experimentally, we have determined that a broad range of activation barriers between 0.5–3.0 eV were necessary to fit the relaxation data.² In addition, these NMR studies show that the annealing process affected over 15% of the carbon atoms. This strongly suggests that no single bond transformation mechanism is responsible for the stress relief. Finally, the NMR data imply (subject to assumptions detailed above) that the fourfold phase is decreasing in volume (4%) with annealing while the threefold phase increases ($\sim 13\%$) in volume. We do not believe that the fourfold phase is in tension, but that the thermal energy provided by annealing allows the fourfold phase to order under the applied compressive stress reducing its volume to relieve strain. The threefold atoms respond by increasing in volume by $\sim 13\%$. The threefold volume change is large, but quite consistent with the high compressibility of graphite perpendicular to the basal planes. These volume changes with annealing appear to contradict the predictions of Kelires.⁵

The inhomogeneous reduction in volume distribution (ordering) experimentally observed with the threefold carbon showing a ~ 5 times larger reduction than the fourfold coordinated carbon can also be compared to the various models. The experimental observed inhomogeneous reduction in local volume distribution (ordering) is probably accompanied by some degree of phase segregation as suggested by the data of Siegal *et al.*;⁷ although the NMR data does not imply a major change in the density of the annealed film as seen in that work. Ferrari *et al.*⁶ have suggested that diffusion of threefold coordinated carbon atoms are activated by annealing. This may be a possibility but experiments looking for diffusion in ta-C materials indicate that higher temperatures are required (>900 °C) to activate diffusion.⁵⁴ Another possibility for phase segregation would be conversion of isolated large volume threefold atoms to smaller volume fourfold thus allowing an entire cluster of fourfold bonded atoms to condense into a more ordered condition. Atoms on the periphery of the cluster would then experience higher tensile strain and perhaps convert to threefold, giving no net hybridization changes. The net result would appear to be diffusion of threefold atoms; consistent with a broad body of evidence showing that clustering of the threefold bonds occurs with annealing.

One last comment related to ordering. We have seen that there is an increase in order due to the narrowing of the NMR peaks, and have demonstrated that this ordering is different for the fourfold and threefold coordinated carbons. We have also observed an increase in the medium range order with annealing.⁵⁵ In fact the amount of change in the NMR spectra appear to be more than what is necessary for complete stress relief, suggesting that the bonding changes are not driven entirely by stress considerations. For example, once clustering of the threefold carbons is initiated into aromatic ring structures, it is probably more likely that additional threefold carbons will be added in a planar arrangement. Near zero stress, this tendency to order could be favored over the energy cost of increased tensile stress. This might explain

why we have found it possible to produce annealed ta-C films with a net tensile stress as high as 300 MPa.

V. CONCLUSIONS

We report solid-state ^{13}C MAS NMR measurements of a stressed ta-C film on a Si substrate and of the bonding evolution with annealing at 650 °C. The most significant change observed in the NMR spectra is the dramatic narrowing of the linewidth of the threefold and to a lesser extent the fourfold coordinated carbon. Since the line widths are inhomogeneously broadened, a significant reordering of the bonding for both species occurs during annealing. The difference spectra between annealed and unannealed films suggest that >15% of the carbon atoms in the structure are affected by these short anneals. No significant change in the fourfold to threefold coordinated carbon ratio is observed during annealing ($\pm 2\%$) indicating that extensive conversion between fourfold and threefold carbons is not responsible for the stress reduction.

We have also shown that the combination of ^{13}C MAS NMR and recent *ab initio* calculations of volume induced variations in ^{13}C chemical shift allow the changes in local atomic volume and volume distribution for ta-C films to be

measured as a function of annealing at 650 °C. In addition, the NMR peak positions shift in a manner that suggests that during annealing the fourfold (threefold) coordinated carbon phase decreases (increases) in volume. The NMR results indicate that there is a reduction in the distribution of atomic volume for the fourfold and threefold coordinated carbons. This reduction is inhomogeneous in nature, with the threefold carbon showing a five times greater reduction in the volume distribution with annealing in comparison to the fourfold carbons. The implications of these measurements for stress relief mechanisms are discussed, and a model for stress relaxation with annealing based on the ordering of both phases is described.

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