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## Dynamic relaxation of the elastic properties of hard carbon films

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# Dynamic relaxation of the elastic properties of hard carbon films

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The effect of enhanced atomic mobility on the growth of hard carbon films was examined. Tetrahedrally bonded amorphous carbon films were deposited by condensing energetic carbon ions using an arc-discharge deposition method. The deposition temperature varied between 50 and 400 °C. The dependence of elastic properties on deposition temperature was examined by determining the frequency-dependent propagation velocity of ultrasonic surface acoustic waves induced by a laser. A remarkable decrease in elastic coefficient was revealed above the deposition temperature of 300 °C and complete relaxation was obtained at 400 °C. This observation was analyzed by using a simple model which was in turn supported by molecular dynamics simulations. The relaxation turns out to be a thermally activated, dynamic process with an activation energy of 0.57 eV. Possible relaxation mechanisms associated with the migration of atoms or defects on a growing surface are discussed. © 1997 American Institute of Physics. [S0021-8979(97)07311-8]

## I. INTRODUCTION

Hydrogen-free hard carbon films are of particular interest because of their high hardness and elastic modulus are achieved using a low-temperature deposition process.<sup>1</sup> In addition to their technological promise, tetrahedrally bonded amorphous carbon (*ta*-C) films pose a number of scientific problems. The major challenge is to understand the atomic interactions during the process of condensation in *ta*-C films. The problem is complicated by the existence of two kinds of carbon-carbon bonds, the  $sp^2$  and  $sp^3$  bonds.

The deposition of *ta*-C films involves energetic ions. The optimum energy window has been shown to lie in a range from about 50 up to 150 eV.<sup>2-4</sup> These energies are far above the thermal energies. Consequently, the growing surface is exposed to an ion bombardment. At the energies employed, carbon ions penetrate into the surface of a growing film to a depth of few atomic layers. During penetration atomic collisions take place which result in interstitials and vacancies. At low temperatures the equilibrium defect concentration is obtained through mutual recombination of point defects below the surface and annihilation at the surface. The timescale of these prompt events after the arrival of an energetic ion is of the order of  $10^{-12}$  s in metals.<sup>5</sup> In the case of a heavy ion bombardment which results in higher densities of vacancies and interstitials there is a phase which is traditionally called the thermal spike. This phase has a duration of about  $10^{-11}$  s and is characterized by energy equipartitioning between atoms involved within a cascade.<sup>5</sup> In the case of a light ion bombardment, such as carbon at low energies, a thermal spike does not develop and the time scale might also be slightly changed due to nonmetallic properties of a substrate.

At higher temperatures the mobility of both defects and atoms is enhanced. This makes long-range diffusion possible. Accordingly, the relaxation phase of the ion impact becomes longer. This has several consequences. Firstly, of course, the longer relaxation phase gives more opportunities for reactions which result in a stable atomic structure. It may also give rise to new mechanisms for atomic migration. If the duration of the relaxation phase is long enough, impact events may overlap. This means that a new ion impact may take place in the vicinity of the migrating ion or defect, creating new defects within an interaction distance from the mobile atoms or defects. Consequently, ion bombardment interferes with the migration of atoms and defects. This in turn has an influence on reactions where an atomic movement is involved. Thus the elongated duration of the relaxation phase is immediately reflected in the atomic structure of the grown films.

In this work we have examined the effect of the atomic mobility (i.e., the substrate temperature) on growth of the *ta*-C films. These measurements provide information about the limits on conditions where a tetrahedral  $sp^3$  hybridization is stabilized and, consequently, helps to understand the factors essential for the condensation of films with a high number of  $sp^3$  bonds. Because of the considerable difficulties in the quantization of electron spectroscopic measurements due to a variation of the sample thickness, for example, we have chosen instead to use elastic properties which can be measured with high accuracy and reproducibility. Elastic properties are assumed to directly reflect changes in the  $sp^2/sp^3$  ratio.

## II. EXPERIMENTAL PROCEDURE AND MEASURED ELASTIC MODULUS

Films were deposited by using an arc-discharge deposition apparatus operating in pulse mode. The pulsed vacuum

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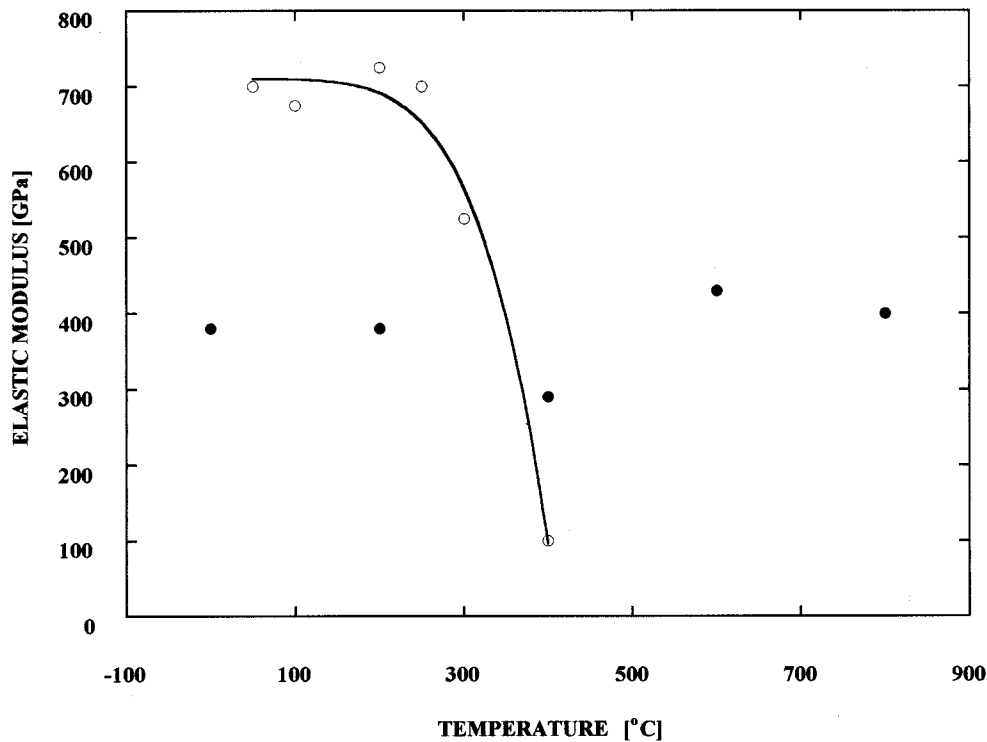


FIG. 1. Measured (○) and simulated (●) Young's modulus as a function of substrate temperature. The solid line is the fitted model.

arc-discharge source was mounted in a 150  $\ell$  vacuum chamber equipped with an oil diffusion pump and operating at a base pressure of about  $3 \times 10^{-4}$  Pa. A cylindrical graphite electrode (diameter 30 mm) was used as a cathode, and a copper cylinder (diameter 150 mm) employed as an anode. The arc was ignited with an electrical spark between ignition electrodes at a frequency of 3 Hz. When discharged, the capacitor bank (2600  $\mu$ F) yielded a current pulse with a maximum of about 3 kA and a half width of 250  $\mu$ s. The nominal rate of deposition was about 0.3 nm/s and an accumulation of about  $1.6 \times 10^{15}$  at/cm<sup>2</sup> was obtained during each pulse. The deposition temperature was controlled using a resistively heated coil, mounted behind the 5-mm-thick copper block which served as the substrate holder. A thermocouple mounted inside was used to monitor a sample temperature.

Assuming singly-charged carbon ions, the ion energy distribution averaged over several sequential discharge pulses was such that the majority of ions had an energy between 40 and 60 eV. A smaller proportion of ions had an energy exceeding 100 eV. An electrostatic detector was used to measure ion energies.

Films were deposited onto Si single-crystal wafers. The average thickness of the deposited films was 100 nm. As-deposited films have an amorphous structure and no  $\pi-\pi^*$  excitation at 7 eV can be observed in the elastic electron loss spectrum, suggesting an abundance of  $sp^3$  bonds. The film deposited at 400 °C had also an amorphous structure as determined with a high-resolution transmission electron microscope but not a detectable number of  $sp^3$  bonds. Details of the microstructural analysis are given elsewhere.<sup>6</sup>

The Young's modulus measurements were based on the determination of the frequency-dependent propagation velocity of ultrasonic surface acoustic waves (US-SAW).<sup>7,8</sup> This allows the nondestructive determination of Young's modulus in thin films to an accuracy of several per cent. In order to carry out measurements a train of elastic surface waves is excited by using the thermoelastic effect of a short laser pulse (0.5 ns pulse length) with a broad frequency range. After a predetermined length of travel, the signal is picked up by a broadband receiver (up to 200 MHz). This procedure is repeated at a different distance by displacing the laser source under the same coupling conditions. Comparison of the Fourier-transformed signals makes it possible to obtain the phase shift and hence the phase velocity. This experimental dispersion curve is approximated by a theoretical one calculated for a coated sample. Use of a suitable curve-fitting procedure allows some of the unknown film parameters (as well as the elastic modulus of the substrate) to be determined.<sup>7,8</sup>

Figure 1 shows the experimentally determined Young's moduli for *ta*-C films deposited at different substrate temperatures. At low temperatures a high value of Young's modulus of about 700 GPa is obtained. It is worth noticing that this figure is significantly higher than that of hydrogenated amorphous carbon films (*a*-H:C). The modulus remains constant up to 250 °C after which relaxation takes place. At a temperature of 400 °C the value of Young's modulus is reduced by almost a whole order of magnitude. It is important to notice that during post-annealing the relaxation of mechanical properties does not occur until a temperature of 600 °C is reached.

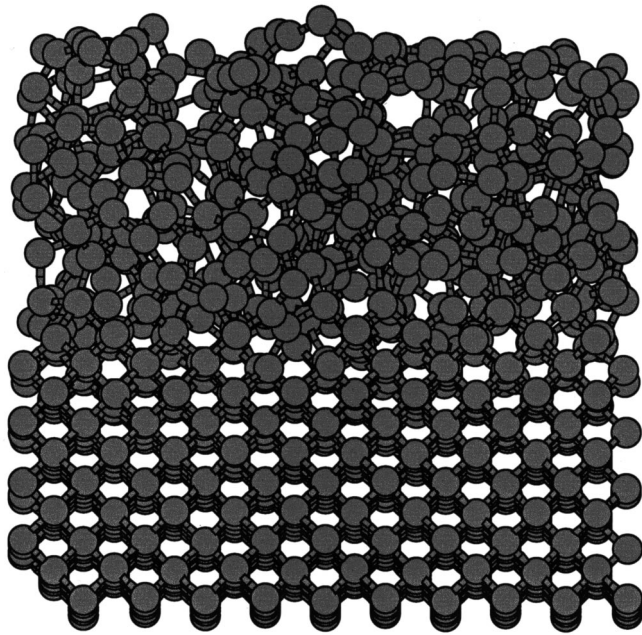


FIG. 2. Simulated structure of amorphous carbon grown at 0 °C onto a diamond substrate.

### III. SIMULATION OF ELASTIC MODULUS

To obtain a more detailed atomic picture of the films, molecular dynamics computer simulations were used to investigate the elastic properties of *ta*-C. The growth of amorphous carbon was studied at five different temperatures (0, 200, 400, 600, and 800 °C). Density and Young's modulus were determined for each of the five samples.

Simulations were performed by depositing 360 carbon atoms one at a time onto an ideal diamond (100) surface consisting of 640 atoms. The kinetic energy of the deposited atoms was 40 eV. The carbon atoms hit the surface perpendicularly.

The diamond (100) substrate consisted of 20 atomic layers, each of which had 32 atoms. Simulations were performed at constant temperature and pressure using the Berendsen method<sup>9</sup> with periodic boundary conditions. The carbon-carbon interactions were described using the classical Tersoff potential.<sup>10</sup> The velocity-Verlet algorithm was used for solving the equations of motion for the atoms. A time interval of  $\Delta t=0.1$  fs was used during the collision of the deposited atom with the surface, otherwise,  $\Delta t$  was kept at 0.5 fs. These time steps were chosen as a compromise between the requirement of the conservation of the energy of the simulated system and the computational cost. The Berendsen cooling algorithm was applied every second time interval except for the final cooling to 0 K, when the thermostat was used at every tenth time interval.

The diamond (100) substrate was allowed to relax for 1.0 ps at the desired growth temperature (0, 200, 400, 600, and 800 °C) at zero pressure. The temperature does not affect the collision phase (which lasts a few ten fs), but governs the long-term relaxation phase. The initial position for the deposited atoms on the plane parallel to the substrate [i.e., (100) or *xy*-plane] was chosen to be random entry point above the surface, beyond the atomic interactions. The time

TABLE I. Densities of the simulated amorphous films grown at different substrate temperatures. The density of ideal diamond in 3.51 g/cm<sup>3</sup>.

Temperature (°C)	0	200	400	600	800
Density (g/cm <sup>3</sup> )	2.54	2.59	2.44	2.44	2.36

interval between subsequent atom depositions was 250 fs, giving a flux density of  $1.23 \times 10^{26}$  atoms/(cm<sup>2</sup> s). This unrealistic high flux density was dictated by the computational limitations. We believe, however, that the essential physics of the growth during collisional phase is captured even with this high flux, since the colliding atoms dissipate their kinetic energy to the surface in a time less than 100 fs.<sup>11</sup> As explained in Discussions the flux used in simulations is a factor of 20 smaller than that required for an overlap the different events with a lifetime of 100 fs. After the growth phase, surfaces were kept at the desired temperature at zero pressure for 1.5 ps. They were then further cooled to 0 K for 1.5 ps in order to avoid temperature fluctuations during the simulated atomic force microscope (AFM) measurements as explained later. An example of the grown surfaces is shown in Fig. 2. More information about MD simulations of the growth of the DLC films<sup>12,13</sup> and theoretical considerations can be found elsewhere.<sup>11</sup>

The density of the amorphous samples was obtained by cutting slices in the *z* direction from the top of the original substrate towards the top of the grown film, stopping at the edge of the surface. The density was then obtained by dividing the total mass of the grown surface by its volume. The number of nearest neighbours, i.e., the bond order for each sample, was also calculated by using a cut-off distance of 2.03 Å (i.e., the first minimum in the pair correlation function). The densities for the grown films are given in Table I. At all growth temperatures the relative bonding proportion for *sp*<sup>2</sup> bonding varied within 63–71% and for *sp*<sup>3</sup> bonding in 22–25%.

To obtain a measure of the elastic-plastic properties of the films grown during the simulations, we employed the technique of simulated nanoindentation by an atomic force microscope (AFM) tip. To the best of our knowledge this work is the first attempt to calculate the Young's modulus directly based on the atomistic MD simulations. The AFM

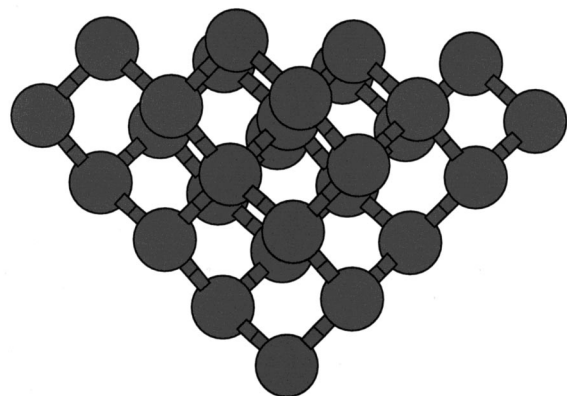


FIG. 3. The AFM tip used in the simulations consisting of a tetrahedral piece of diamond with 28 atoms.

tip is a tetrahedral 28-atomic pyramid-like piece of ideal diamond, Fig. 3. It was brought above to the nearest-neighbor distance 2.8 Å from the surface, pushed down 4 Å into the amorphous sample in the ( $-z$ ) direction and then pulled back to its initial position. The tip was moved 0.001 Å in each time interval ( $\Delta t=0.5$  fs). Four AFM simulations were made for each of the five samples starting from different positions on the  $xy$  plane [(100) plane]. The scaled (i.e.,  $0 \leq x < 1$  and  $0 \leq y < 1$ )  $xy$  positions are given in Table II. The same AFM measurements were also performed for an ideal diamond (100) surface in order to obtain a reference system. During the simulations the penetration depth  $z$  and the normal force  $F_z$  acting on the tip were recorded at each time interval. Figure 4 shows a typical loading-unloading curve for diamond. Based on this, values for Young's modulus were calculated for each amorphous film sample grown as described above. Young's modulus  $E$  was approximated as<sup>14</sup>

$$E = \frac{\sqrt{\pi}(1-\nu^2)}{2\sqrt{A}} \frac{dF_z}{dz}, \quad (1)$$

where  $\nu=0.104$  is the Poisson ratio of diamond<sup>15</sup> and  $A$  is the effective contact area. The slope of the unloading curve  $dF_z/dz$  in Fig. 4 was calculated while the tip was being pulled back from 0.1 to 0.5 Å after its deepest penetration. For ideal diamond we set the Young's modulus to its experimental value of 1050 GPa<sup>15</sup> and thus obtained an effective value for the contact area  $A=0.942$  (Å<sup>2</sup>), this was then used to calculate  $E$  for the amorphous films. In a real AFM experiment the contact area is of the order of 100 Å<sup>2</sup>, and the penetration depth of the tip into the sample is typically more than 100 Å.<sup>14</sup>

The calculated values of Young's modulus  $E$  for each film and tip position are shown in Table II. The AFM measurements are very sensitive to the local structure of the film and thus to the tip position. For example, values for ideal diamond may differ from each other by almost 30% depending on whether the tip is located above a carbon atom or above the center of the two carbon atoms situated in the outermost surface layer.

Comparing the experimental values of Fig. 2 with the simulated ones in Table II reveals two differences. Firstly, the measured experimental value of Young's modulus for films deposited at low temperatures is almost twice as high as the value resulting from the simulations. Secondly, as

could be anticipated from the density values of the simulated pure carbon films grown at different temperatures, no significant dependence of  $E$  on substrate temperature was observed. We attribute these differences to many different sources. Firstly, the difference in Young's modulus at low deposition temperatures may be due to the classical potential which inadequately describes the growth process. Secondly, our simulations last less than  $10^{-9}$  s. In this time we can adequately follow the deformations and the relaxations due to the single collision cascades. The duration of these cascades is estimated to be of order  $10^{-13}$  s. We cannot, however, be certain that we have observed all the thermal relaxations, because the time required to reach the thermal equilibrium is up to  $10^{-10}$  s. Furthermore the diffusion of vacancies and long-range rearrangements of the atom structures in a DLC film may take even seconds.<sup>11,16</sup> These relaxations are totally inaccessible with our method. Finally, we have neglected the contribution of the AFM cantilever to the potential energy of the system. A harmonic potential for the elastic energy of the cantilever is given in a simulated AFM measurement of graphite by Tsukada *et al.*<sup>17</sup> We also recommend other studies relevant for the AFM-tip-surface interactions.<sup>18,19</sup>

#### IV. ACTIVATION ENERGY OF THE RELAXATION OF THE ELASTIC MODULUS

Bearing these experimental and simulated results in mind we have used the following physical model to analyze our observations. Let us assume (as explained on the basis of the simulation results above) that even at elevated temperatures the same relative fraction of carbon atoms,  $n_{sp^2}^0$ , is  $sp^2$  bonded immediately after the prompt impact events (the period of time covered by the simulation). If the amount of carbon which will be bonded to the structure by  $sp^2$  bonds increases during the relaxation phase at elevated ambient temperature by amount of  $\Delta n_{sp^2}$  the relative fraction of  $sp^2$  bonded carbon in the final structure,  $n_{sp^2}$ , can be deduced from the equation

$$n_{sp^2} = n_{sp^2}^0 + \Delta n_{sp^2}. \quad (2)$$

In order to relate the observed elastic properties to the relative abundance of  $sp^2$  and  $sp^3$  bonds we assume a simple rule-of-mixture

$$E = n_{sp^2} E_{sp^2} + n_{sp^3} E_{sp^3}, \quad (3)$$

TABLE II. Calculated Young's modulus (GPa) for the simulated amorphous films grown at different temperatures. The Young modulus was measured at four tip  $xy$  positions for each sample as indicated with scaled coordinates in the table.

	Tip position (scaled coordinates)				Average
	(0.00, 0.00)	(0.25, 0.25)	(0.50, 0.50)	(0.75, 0.75)	
Diamond	868.7	1218	1210	878.9	1050
$T=0$ °C	274.6	545.5	327.0	385.4	380
$T=200$ °C	328.8	595.8	228.7	347.0	380
$T=400$ °C	190.7	334.6	216.0	420.3	290
$T=600$ °C	525.5	426.3	475.9	310.4	430
$T=800$ °C	619.7	275.3	297.5	395.3	400

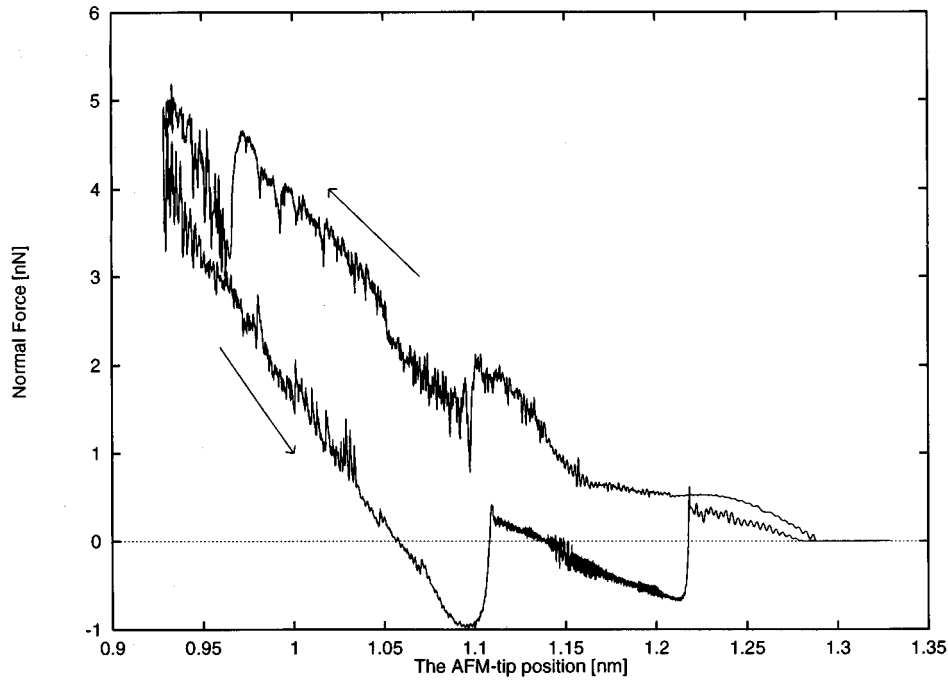


FIG. 4. A loading-unloading curve for a simulated indentation measurement on a simulated amorphous surface grown at 0 °C.

where  $E$  is the elastic constant of the material with the fractions of  $sp^2$  and  $sp^3$  bonds  $n_{sp^2}$  and  $n_{sp^3}$ , respectively.  $E_{sp^2}$  and  $E_{sp^3}$  are the elastic constants of materials which are formed completely of  $sp^2$  and  $sp^3$  bonds. Combining Eqs. (2) and (3) yields

$$E = (1 - n_{sp^2}^0)E_{sp^3} + n_{sp^2}^0 E_{sp^2} + (E_{sp^2} - E_{sp^3})\Delta n_{sp^2}. \quad (4)$$

The first two terms of Eq. (4) represent the Young's modulus obtained on films deposited at low temperatures. The third term of Eq. (4) represents relaxation which occurs at elevated temperatures. This relaxation begins after the collisional phase (about  $10^{-10}$  s) and may last even seconds because a long-range migration is involved. Now if the rate of the relaxation reaction is controlled by a thermally activated process, as is evident according to the experimental results obtained,  $\Delta n_{sp^2}$  can be expressed as

$$\Delta n_{sp^2} = \Delta n_{sp^2}^0 \exp(-Q/kT), \quad (5)$$

where  $Q$  is the activation energy of the transformation process,  $k$  the Boltzmann constant,  $T$  is absolute temperature, and  $\Delta n_{sp^2}^0$  the pre-exponential factor. No assumption is made about the nature of the relaxation process at this stage. It is not necessary to know explicitly the duration of the relaxation phase either. After substitution of Eq. (5) into Eq. (4) the elastic constant predicted by the model can be fitted into the experimental elastic constants as a function of the deposition temperature. In Fig. 2 the fitted curve is shown together with the experimental data. Good agreement can be seen. The value of 0.57 eV was obtained for the activation energy  $Q$ . To the best of our knowledge this is the first time the activation energy of a relaxation during the deposition of

diamond-like films have been determined. This value is physically acceptable and of the order of thermally-activated atomic or defect migrations.

## V. DISCUSSION

It is evident, based on two experimental observations, that the thermally-activated relaxation in the structure of  $ta$ -C films occurs during deposition at elevated substrate temperatures. Firstly, in this work a strong dependence of the elastic modulus on ambient temperature was observed. Secondly, the relaxation in the elastic modulus occurs at significantly lower temperatures than relaxation during post-deposition annealing. This clearly shows that the relaxation is dynamic in nature and associated with the conditions prevailing during condensation. If we assume that atomic migration is involved in the relaxation process, we have at least two different possibilities. Firstly, arriving carbon atoms are not chemically bonded at all immediately after impact, but exist as ad-atoms on the surface. Accordingly, ad-atoms therefore have adequate time to find an equilibrium location because of their enhanced mobility. This model explains the difference in temperatures associated with the relaxation of mechanical properties during deposition and post-annealing, because the temperature required to break the bonds of chemically-bonded carbon atoms and make them mobile is definitely higher than the temperature at which ad-atoms are mobile. The model does not explain, however, the abundance of  $sp^3$  bonds in structures condensed at low temperatures. It is also in conflict with the simulation results which show an unchanged relative fraction of  $sp^3$  bonds during a short period of time, even at the elevated substrate temperatures.

For these reasons and on the basis of our observations we propose a model where carbon atoms, with appropriate energy, are first condensed into a structure with an abundance of  $sp^3$  bonds, i.e., are  $sp^3$  bonded. A proportion of these carbon atoms are displaced by the constant ion bombardment by incident atoms (this of course also occurs at low deposition temperatures). At elevated temperatures, displaced carbon atoms and defects generated by the ion bombardment are more mobile, and are assumed to be mobile for longer periods of time as explained above. A question still remaining is whether there is interaction between the displaced, migrating carbon atoms and the ion bombardment, i.e., is there an overlap of impact events. This would make radiation-enhanced diffusion a more likely mechanism for the relaxation. If the projected area of an impact event is  $A$  and the time constant for relaxation is  $\tau$ , the probability of overlap within  $\tau$  is  $1 - \exp(-\tau AF)$ , where  $F$  is the incident particle flux.<sup>20</sup> For considerable overlap  $\tau AF > 1$ . If we assume the area  $A$  to be  $38 \text{ \AA}^2$  (Ref. 21) and  $\tau$  to be  $100 \text{ fs}$ <sup>11</sup> the flux required for overlap to occur is as high as  $2.6 \times 10^{27} \text{ ions/cm}^2 \text{ s}$ . This cannot be obtained in practical conditions and it is even a factor 20 higher than used in the simulations in this work. On the other hand, in the arc-discharge deposition  $10^{15} \text{ ions/cm}^2$  are deposited during a single pulse with a duration of  $250 \text{ \mu s}$ . In order to achieve overlap, the relaxation time should be  $65 \text{ \mu s}$ . Although molecular dynamics calculations on metals, e.g., copper, show that the duration of the relaxation phase which immediately follows the collision phase increases with increasing ambient temperature, the time constants are still in the picosecond range.<sup>22</sup> In the regime of radiation enhanced diffusion (RED), lifetimes are assumed to be sufficient long for the conditions for the overlapping of impact events to occur.

The activation energy  $0.57 \text{ eV}$  deduced from the temperature dependence of the elastic constant can be compared to the values for activation energies of possible atomic processes at the growth surface. The migration energies for a vacancy ( $E_{VM}$ ) in diamond and graphite are  $1.9$  and  $1.6 \text{ eV}$ , respectively.<sup>23</sup> Vacancies are associated with crystalline structures and should be used with caution as the  $ta$ -C films have an amorphous microstructure. At least part of carbon ions have energies above the displacement energy in diamond, about  $40 \text{ eV}$ ,<sup>24</sup> this results in the formation of displaced atoms. The values given above for the migration energy of vacancies in diamond and graphite are too high compared to the experimental activation energy of the relaxation,  $0.57 \text{ eV}$ . The activation energy  $Q_{RED}$  of RED in the case of defect annihilation by direct recombination of vacancies and interstitials is  $Q_{RED} = 0.5 E_{VM}$ .<sup>25</sup> In the case of diamond and graphite this yields values of  $0.95$  and  $0.8 \text{ eV}$ , respectively. These are higher than the observed value  $0.57 \text{ eV}$ , but they are of the same magnitude. One should also remember that this is atomic migration in the very shallow regime at the surface, and this could change the activation energies. Furthermore, on the basis of the current observations the possibility of surface diffusion, or ion bombardment-assisted surface diffusion, cannot also be ruled out. Moreover, the formalism of the present model is still valid if instead of a migration of radiation induced point

defects a migration of an incident, depositing ion is concerned under an ion bombardment.

The growth of  $ta$ -C films from energetic ions can also be explained using a subplantation model.<sup>26–29</sup> In this model carbon ions are implanted below a surface. Relaxation phenomena observed in the past, e.g., as a function of the increasing energy of incident ions,<sup>4</sup> is explained on the basis of diffusion. In this piece of work we have determined the activation energy for such a diffusion-controlled relaxation. It should be also noticed that in previous studies the relaxation in diamond-like films during deposition occurs at significantly lower temperatures, e.g., at  $150 \text{ }^\circ\text{C}$ .<sup>30</sup> We speculate that other relevant deposition parameters such as deposition rate play a role in the relaxation. The studies concerning this matter are now in progress.

One other interesting result can be extracted from our analysis. In Eq. (4) the first two terms on the right present to Young's modulus of unrelaxed material, e.g., in our case about  $700 \text{ GPa}$  (Fig. 2). If we use the value of  $1050 \text{ GPa}$  for Young modulus for material with  $100\% sp^3$  bonds<sup>11</sup> and  $100 \text{ GPa}$  for a completely relaxed material with  $100\% sp^2$  bonds (based on our experimental result in Fig. 2), we can calculate that a material with Young's modulus of  $700 \text{ GPa}$  should contain  $63\% sp^3$  bonds. This is a reasonable value and consistent with those reported for unrelaxed  $ta$ -C films.<sup>4</sup> On the other hand, in the simulation, the abundance of  $sp^2$  bonds varied from  $63$  to  $71\%$ , the average figure being  $67\%$ . If we use these values together with the Young's moduli for materials with  $100\%$  of  $sp^3$  and  $sp^2$  bonds as given above, the value of  $414 \text{ GPa}$  is obtained for a material with  $67\% sp^2$  bonds. This is in a reasonable agreement with the simulated values in Table II. Thus the "rule-of-mixture" seems to be a reasonable description of the elastic modulus of a material with a combination of  $sp^3$  and  $sp^2$  bonds.

As a by-product we found that simulated AFM measurements turned also to be a very sensitive probe for the local structure of a surface, this is shown by the results in Table II. In the future, it might be possible to deduce some local properties such as a ring structures and bond order from the AFM data.<sup>31</sup>

## VI. CONCLUSIONS

In conclusion we can say that on the basis of our experimental observations the relaxation of the elastic modulus in  $ta$ -C films at elevated substrate temperatures is dynamic in nature. This relaxation is associated with the conditions in the vicinity of the condensing atoms and may also be affected by the bombarding effect of incident carbon ions. A model, which is supported by molecular dynamic simulation, suggests that immediately after arrival the number of carbon atoms which are bonded with  $sp^3$  bonds is independent of temperature within the temperature range involved in this work. When applied to the experimental data, this model yields an activation energy of  $0.57 \text{ eV}$  for the relaxation. This is physically acceptable and of similar magnitude to the processes which include the migration of atoms or defects. The thermally activated processes seem to be effected by the ion bombardment.

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