Growth Mechanism and Cross-Sectional Structure of Tetrahedral Amorphous Carbon Thin Films

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Spatially resolved electron energy loss spectroscopy is used to characterize the cross-sectional structure of highly tetrahedral amorphous carbon films, particularly concentrating on the sp^2 bonded surface layer. The surface layer is shown to be due to subsurface conversion from sp^2 to sp^3 bonding at the depth of carbon ion implantation during film growth. The thickness of the surface layer is used as a measure of the ion penetration depth, varying from 0.4 ± 0.2 nm for 35 eV ions to 1.3 ± 0.3 nm for 320 eV ions. The influence of growth temperature is investigated, and it is found that the temperature above which sp^3 bonding is not stable is greatly reduced in the region affected by ion bombardment. [S0031-9007(98)05863-3]

Tetrahedral amorphous carbon (ta-C) is a form of amorphous carbon with greater than 80% tetrahedral (sp^3) bonding which can be deposited as a thin film from a plasma of carbon ions [1]. It is generally accepted that the mechanism promoting sp^3 bonding over the normally more stable trigonal planar (sp^2) structure for amorphous carbon is related to shallow implantation of low energy (20–500 eV) ions [1–3]. The energy dependence of the sp^3 fraction has been explained qualitatively in terms of a balance between implantation (subsurface growth) and relaxation [4], the relaxation being described by a thermal spike model. The same model has been used to describe the formation of compressive stress by ion bombardment [5]. Although the precise details of the implantation and relaxation processes remain unclear, the film is predicted to be sp^2 bonded near the surface above the depth at which subsurface conversion to the denser sp^3 bonded structure occurs. Recently, spatially resolved cross-sectional electron energy loss spectroscopy (EELS) has verified the existence of a thin (~ 1 nm) layer of sp^2 bonded carbon at the surface of a ta-C [6].

In this Letter, the bonding and composition of ta-C films are investigated using spatially resolved cross-sectional EELS, paying particular attention to the sp^2 bonded surface layer. It will be shown that this surface layer is an intrinsic feature of the film growth and is related to the interaction of the bombarding ions with the growing film. The interaction of the ions with the growing surface and the conversion of sp^2 to sp^3 bonded material will be investigated as a function of the ion energy and the growth temperature.

The ta-C films studied here were deposited in a filtered cathodic arc apparatus which has been described in detail elsewhere [7,8]. Briefly, a cathodic arc discharge on a 99.995% pure graphite cathode was used to produce a highly ionized carbon plasma. A curved solenoidal magnetic field guides the plasma around a 90° bend in order to eliminate macroscopic particles of graphite which

are also emitted by the arc. The films were deposited on silicon (001) wafers which had been ultrasonically cleaned in acetone. The base pressure of the vacuum system was better than 10^{-4} Pa, although the pressure rose to about 10^{-3} Pa during deposition. The substrate was effectively masked during a transient pressure increase, which occurred in the initial seconds of arcing, by turning off the curved solenoid magnetic field.

Cross-sectional specimens for scanning transmission electron microscopy (STEM) were made by backgrinding and polishing the coated silicon substrate to a thickness of about 0.1 mm prior to cleaving 90° wedges, which were mounted on copper supports and viewed edge-on [9]. The method is rapid and avoids problems with contamination and ion bombardment-induced structural changes.

In this Letter, two systems were used for the collection of spatially resolved EELS line profiles. The first system was a VG501 STEM with a nominal probe size of 0.4 nm and a Gatan imaging filter which allowed <1 eV energy resolution (required for accurate sp^3 fractions) simultaneously with a 500 eV wide energy range for compositional analysis. The second system was a VG601 STEM with a probe size verified to be less than 0.3 nm (by high resolution annular dark field images) and a Gatan 666 parallel EELS which required separate line scans for sp^3 fractions and specimen composition. Otherwise, EELS profiles were obtained as described previously [6]. Briefly, for each line scan a series of 50–100 EELS spectra were recorded at intervals of 0.2–0.5 nm. Typical acquisition times were 0.5–2 s per spectra, and a collection angle of approximately 15 mrad were used. Standard procedures [10] were used to determine elemental densities from the absorption edge areas, and the sp^3 fraction was found from the area of the $1s$-π^* pre-edge relative to the carbon $1s$ absorption, using polycrystalline graphite as a standard [11].

The variation of the sp^3 fraction and the area densities of carbon, silicon, oxygen, and calcium across a cross

section of a ta-C film which was deposited with an ion energy of 320 eV are shown in Fig. 1. The leftmost region is the silicon substrate. A peak in the oxygen density next to the substrate is due to the presence of a thin oxide layer on the silicon substrate prior to film growth. In addition to silicon and oxygen, this layer contains a significant amount of carbon. The silicon L edge structure (near edge) in this layer was typical of substoichiometric silicon dioxide [6,12]. Although the carbon K edge was too noisy for reliable evaluation of the sp^3 content, a clear π^* peak was observed, suggesting that the carbon in this layer was primarily sp^2 bonded. In the next 4–5 nm, the silicon density rapidly drops below the detection limit while the carbon density increases to its maximum value and the oxygen density decreases slowly. The structure of the silicon-1 edge here suggests that the silicon is bonded to carbon rather than oxygen [6]. The carbon sp^3 fraction is initially 10%–20% before increasing to 80%–90% 5 nm from the edge of the silicon oxide layer. The bulk of the ta-C film contains 100% carbon, with no detectable impurities and approximately 90% sp^3 bonding. Just below the surface of the film, which is marked by a sharp decrease in the carbon density, there is a rapid decrease in the sp^3 fraction which we attribute to a 1.3 ± 0.3 nm thick layer which is primarily sp^2 bonded carbon. This layer contains no detectable impurities and is clearly distinguishable from the oxygen and calcium-containing contamination layer above it. The surface layer can also be distinguished as a low density layer, distinct from any contamination, using both Fresnel contrast and annular dark field imaging, and we have observed this repeatedly in a wide range of ta-C specimens.

The composition and bonding through the thickness of a ta-C film deposited with a significantly lower carbon ion energy of 35 eV is shown in Fig. 2. Again the sp^3 fraction decreases just below the surface of the film because of the presence of an sp^2 bonded surface layer. In this case, the surface layer is only 0.4 ± 0.2 nm thick. A layer with a reduced sp^3 fraction is also seen near the interface with the silicon substrate. In contrast with the 320 eV case, the initial low sp^3 layer is comparable in thickness to the surface layer and the extent of mixing of oxygen into the carbon film is also greatly reduced. This cause of the low sp^3 fraction in the initial stage of growth is not clear, although it may be related to the presence of oxygen from the substrate in this layer. In any case, it is evident from Figs. 1 and 2 that both the thickness of the sp^2 bonded layer and the mixing of the film and substrate materials increase dramatically with the ion energy.

Our results show that the sp^2 bonded surface layer does not form after the film growth, but instead is present during the growth of the sp^3 bonded material. That is, as the film grows, the bottom part of the sp^2 bonded layer is converted to sp^3 bonding by a subsurface deposition process and the top of the sp^2 bonded layer expands away form the substrate. If the surface layer is formed
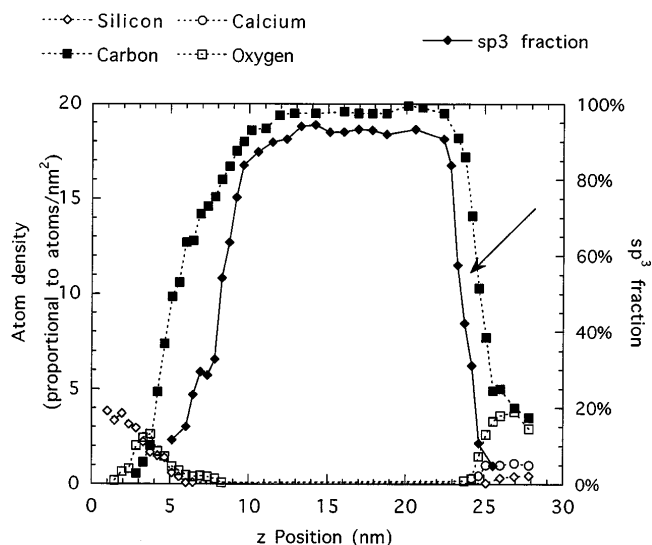

FIG. 1. The sp^3 fraction and the carbon, silicon, and oxygen, and calcium densities (units proportional to atoms per unit area) obtained from EELS spectra in a VG501 STEM as a function of distance across a cross section of a ta-C film deposited from 320 eV carbon ions. The sp^2 bonded surface layer is highlighted with an arrow.

after deposition then interruptions in the deposition would result in buried sp^2 bonded layers. While maintaining the films in the vacuum system, the deposition of the film in Fig. 1 was interrupted three times, each time for some minutes, but no buried layers were seen. The deposition of the film in Fig. 2 was interrupted for nearly two hours, and this has resulted in a small dip in the sp^3 fraction midway through the film. The small dip is attributed to the effect of gases arriving from the vacuum system (10^{-4} Pa), since a brief exposure of the
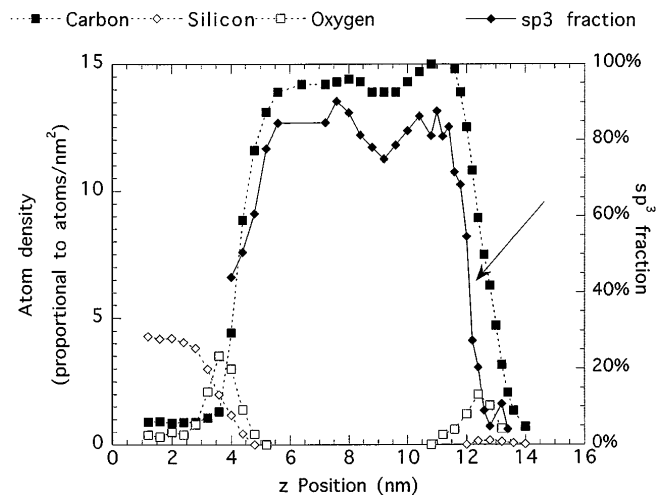

FIG. 2. The sp^3 fraction and the carbon, silicon, oxygen, and calcium densities (units proportional to atoms per unit area) obtained from EELS spectra in a VG501 STEM as a function of distance across a cross section of a ta-C film deposited from 35 eV carbon ions. The sp^2 bonded surface layer is highlighted with an arrow.

film to air gives a much clearer buried sp^2 layer [6]. Furthermore, if the surface layer forms subsequent to deposition then it should re-form if removed. We find that, after exposure of a ta-C film to a low pressure oxygen plasma (sufficient to remove several nanometers of material), the sp^2 bonded surface layer can no longer be detected using EELS, Fresnel contrast imaging, or annular dark field imaging. The removal of the surface layer using an oxygen plasma has been used to enable fabrication of a thin film transistor in which ta-C is the active material [13].

The fact that an sp^2 bonded surface layer is present during deposition of primarily sp^3 bonded films requires conversion of sp^2 bonding to sp^3 bonding below the surface of the growing film. This subsurface conversion may be driven by the thermodynamic favoring of sp^3 bonding under the large compressive stresses (typically, 5 GPa) present in these films, as suggested by McKenzie et al. [1]. Recent experimental data from ta-C films containing boron show that the absolute stress value can be reduced to 2 GPa while maintaining 80% sp^3 bonding [14]. These results are in keeping with those obtained from ab initio structure simulations of ta-C, where it was found that a net compressive stress existed in a-C films with a high sp^3 bonded fraction, though the stress value averaged over all carbon sites was not necessarily high [15]. Alternatively, Robertson [2,4] has suggested that shallow implantation of carbon ions results in an increased atom density which forces the transformation from sp^2 to sp^3 bonding. In either case, the sp^2 to sp^3 conversion should happen close to the depth at which the energetic species are buried. That is, the surface layer thickness should depend on the interaction of the low energy ions with the surface of the growing film.

Figure 3 shows the dependence of the surface layer thickness on the energy of the carbon ions. We believe that this is the first measure of the implantation depth for ions in this energy range. The conversion of the sp^2 surface layer to an sp^3 rich layer will occur on either side of the characteristic implantation depth of the low energy C^+ ions. This is due to there being some knock-on of the ions beyond the position at which an implanted carbon ion comes to rest. There is therefore a region of density increase and atomic reordering surrounding the characteristic implant depth. There is some uncertainty in the relation between the conversion layer thickness and implantation depth at these low energies and this is probably of the order of 0.2–0.4 nm, as shown in Fig. 3. Even at the extreme of this uncertainty (0.6 nm at 35 eV to 1.6 nm at 350 eV), the results shown in Fig. 3 are far smaller than previously predicted from calculations. For comparison, computer simulations using the TRIM computer program performed by Lifshitz et al. [16] give a range for C^- into graphite of 1 nm at 35 eV, increasing to 4 nm at 350 eV, substantially larger than the observed surface layer thicknesses. On the other hand, molecular dy-
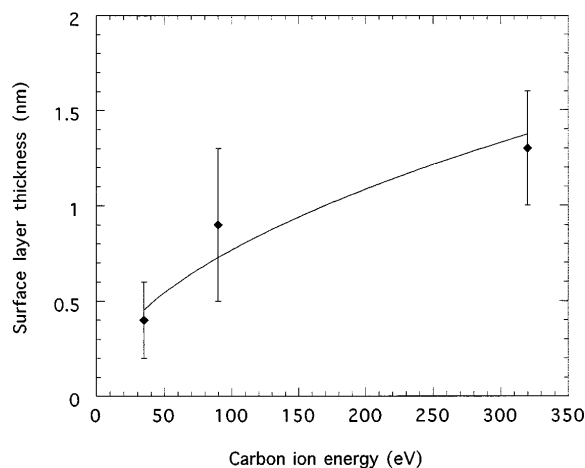

FIG. 3. Thickness of the sp^2 bonded surface layer as a function of the carbon ion energy. The energy distribution of the ions has a FWHM of 8 eV [18].

namics simulations of film growth with ion energies in this range show that ions rarely penetrate more than one monolayer (<0.5 nm), substantially less than the observed layer thickness [17]. The discrepancy between the calculated ion ranges and the measured surface layer thickness is not surprising. TRIM calculations rely on cross sections which are obtained by extrapolating measured cross sections from much higher energies, while molecular dynamics simulations use interaction potentials derived from spectroscopic measurements at thermal energies.

The effect of the substrate temperature during deposition has been examined for ta-C films deposited from 90 eV carbon ions. We find that a film deposited at 200 °C has the same surface layer thickness as a film deposited at room temperature, namely, 0.9 ± 0.4 nm. That is, the thickness of the surface layer is not influenced by the deposition temperature. This suggests that the surface layer is controlled entirely by ion bombardment and is not affected by thermally driven diffusion processes. Further, since the film-substrate mixing depth can be greater than the surface layer thickness (see Fig. 1), it suggests that atom transport can occur on scales larger than the surface layer thickness. The fact that we measure surface layers smaller than this mixing layer at the substrate, which is characteristic of the ion mixing/transport depth, leads us to argue that subsurface sp^2 to sp^3 conversion is a distinct process from mixing due to ion transport. Surface layer thickness is then solely determined by the ion implantation depth.

Previous work has shown that in this deposition system the average sp^3 fraction rapidly decreases below 10% for deposition temperatures above approximately 250 °C [18]. A similar transition has been reported by Lifshitz et al. [3], but at a lower temperature of 150 °C. The cross-sectional variation of the sp^3 fraction for a film deposited at a temperature of 300 °C is shown in Fig. 4. The decrease in sp^3 fraction through the thickness of the film is attributed to a temperature increase which occurs
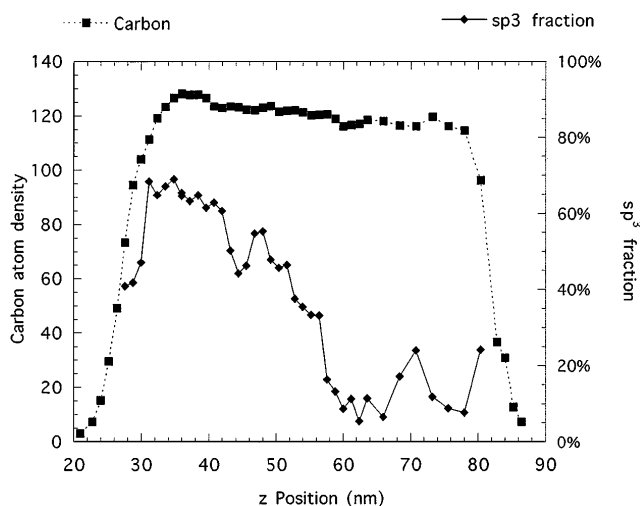
FIG. 4. The sp^3 fraction and the carbon density obtained from EELS spectra in a VG601 STEM as a function of distance across a cross section of a ta-C film deposited from 90 eV carbon ions on a substrate held at a temperature of 300 °C. Film growth is in the direction of increasing z.

during deposition due to heating of the surface by the ion bombardment. That is, for the initial stage of the film growth the surface temperature is 300 °C, but during deposition the film temperature increases by 70–90 °C [18]. The fact that the sp^3 fraction is higher at the bottom of the film indicates that, once formed, conversion of sp^3 to sp^2 does not occur in this temperature range. This is consistent with our observation that the sp^3 fraction was unchanged when we heated a ta-C film to 650 °C in vacuum after deposition. The reduced sp^3 fraction in the upper part of the film must then be due to the increased deposition temperature *in combination* with the ion bombardment. That is, above approximately 300 °C the implantation of carbon ions no longer causes conversion of sp^2 bonding to sp^3 bonding.

Electron diffraction from the film deposited at 300 °C viewed in cross section shows two diffuse spots at the (002) angle. The presence of diffuse (002) reflections implies a layered graphite structure, although with disordered layer stacking. The orientation of the (002) spots is consistent with the majority of graphitic material having the c axis in the plane of the film (i.e., graphite layers stand perpendicular to the substrate). That is, above the transition temperature, not only is sp^2 not converted to sp^3 bonding at the implantation depth but the resulting sp^2 bonded film shows substantially more long range (>1 nm) order than the amorphous ta-C material produced below the transition temperature. We attribute the improved order to increased atom mobility in the region of the ion bombardment. Given that below 300 °C amorphous sp^3 material is obtained at much higher ion energies (e.g., 320 eV), the increased atom mobility and the absence of sp^2 to sp^3 conversion cannot be due to the ion energy alone. Instead, we suggest that the growth temperature (~0.05 eV) has a strong effect on the processes following ion implantation, despite being small compared to the ion energy. That is, these results provide strong evidence for mobility (diffusion) of an atom after subsurface implantation, and that it is the temperature effect on this diffusion/mobility process which prevents the sp^2 to sp^3 conversion. The background thermal "noise" is therefore very important in terms of influencing carbon atom mobility, and as a consequence sp^3 bond formation, immediately following ion implantation.

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