Investigation of local ordering and electronic structure in Si- and hydrogen-doped tetrahedral amorphous carbon thin films

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This work investigates the C K-edge near-edge x-ray absorption fine structure (NEXAFS) and x-ray reflectivity spectra of Si- and hydrogen-incorporated tetrahedral amorphous carbon (ta-C:Si:H) films. The C K-edge NEXAFS spectra indicate that the sp^2/sp^3 hybridization ratio increases with the amount of tetramethylsilane vapor precursor introduced during deposition. This suggests that Si addition enhances sp^2- and reduces sp^3-bonding configurations. The increase in sp^2 sites correlates well with the decrease in hardness, mass density, and thermal stability. The comparison of angle-dependent NEXAFS spectra of nondoped and Si-doped ta-C films at the K edge reveals significant dopant-induced local ordering in $\pi^*_{C=C}$ and σ^*_{C-H} orbitals. In contrast to the highly oriented pyrolytic graphite, the $\pi^*_{C=C}$ orbitals lie parallel to the surface. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2149173]

The addition of alloying elements, such as silicon, has been found to release the residual stress and improve the properties in amorphous carbon (*a*-C) films.[1,2] However, very little work has been reported on the resulting electronic structure responsible for the induced changes. This letter focuses on the study of the electronic structure (i.e., π orbital state and its orientation), and structural properties of ta-C:Si:H films synthesized by the filtered cathodic vacuum arc (FCVA) technique. In particular, the role of tetramethylsilane [Si(CH$_3$)$_4$, TMS] as a hydrogen-rich Si precursor gas is explored.

The C K-edge near-edge x-ray absorption fine structure (NEXAFS) and x-ray reflectivity (XRR) measurements of as-grown tetrahedral amorphous carbon (ta-C) and ta-C:Si:H films were performed respectively at stations 2.1 and 2.3 of the Synchrotron Radiation Source facility at Daresbury Laboratory, UK. The NEXAFS data were acquired using surface sensitive total-electron yield mode. The angle of incidence (the angle between the sample surface and the x-ray beam) of the light beam was kept at 55°, (the magic angle) to avoid orientation effects on the π^* state intensity, except when performing angle-dependent study. Nanoindentation tests were performed with a MTS nanoindenter *XP* system.

Figure 1 shows the normalized C K-edge absorption spectra of ta-C:Si:H films as a function of Si concentration, together with that of a graphite sample. All spectra were normalized to the maximum intensity and shifted to each other for clarity. The inset presents the difference curves of the resonance peak located at 285.3 eV, $\pi^*_{C=C}$, between ta-C and that of ta-C:H:Si samples. One can observe the evolution of this peak with the increase of Si concentration. Since this difference peak can be taken as a measure of sp^2 hybridized bonds in the films,[3] this evolution implies that the sp^2 content increases (i.e., graphitization tendency) with the Si-addition process (i.e., raising the TMS flow rate).

Visible-Raman spectra of ta-C:H:Si samples exhibited an ascending slope (figure not presented). We observed a similar

behavior in Si-incorporated hydrogenated amorphous carbon films deposited in a plasma-enhanced chemical vapor deposition (PECVD) reactor using a mixture of C$_2$H$_2$/TMS plasma.[4] A hydrogenation process was established by heavy-ion elastic recoil detection technique, which was used to directly estimate the hydrogen content in the PECVD films. A similar hydrogenation process is to account for the ascending slope in the visible Raman spectra of FCVA films and is attributed to the use of TMS precursor gas in the Si-incorporation process.

To further confirm the hydrogenation phenomenon in ta-C:H:Si films, an *in situ* rapid thermal annealing (RTA) experiment has been carried out. Figure 2 illustrates the C K-edge absorption spectra of pure and Si-incorporated (20 at. % Si) ta-C films before and after annealing at 650 °C for 2 min using an electron-beam heating approach. The
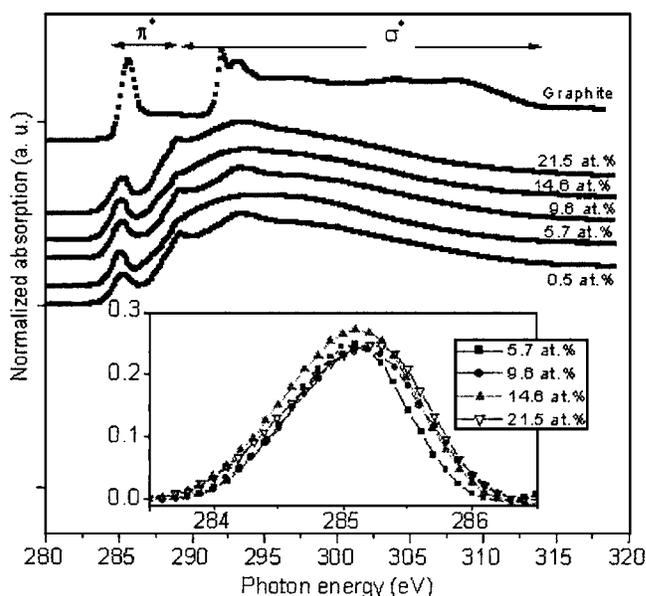

FIG. 1. (a) Normalized C K-edge NEXAFS spectra of FCVA ta-C:H:Si films and a graphite sample. The inset presents the difference curves between the spectra of the ta-C and ta-C:H:Si films.

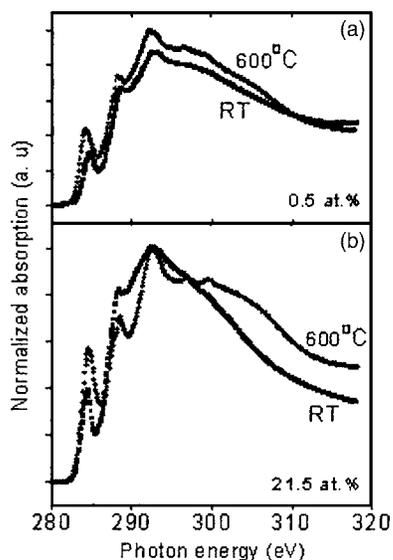[a]Author to whom correspondence should be addressed; electronic mail: g.abbas@ulster.ac.uk

FIG. 2. Normalized C K-edge NEXAFS spectra of RTA ta-C and ta-C:H:Si (20 at. % Si) films.

FIG. 4. (a) X-ray specular reflection profiles of pure and Si-incorporated (20 at. % Si) ta-C films illustrating the experimental and a model fit curves. (b) Evolution of mass density of ta-C:Si:H films with Si content.

π^*/σ^* peak ratio increased from 0.25 to 0.35 and from 0.35 to 0.6 for the ta-C and ta-C:H:Si samples, respectively. This indicates a graphitization trend in the ta-C:H:Si films, which becomes more prominent with annealing. It is well known that the hydrogen content in hydrogenated a-C films decreases upon thermal treatment and films undergo a structural transition toward a disordered graphitic material.[5] On the other hand, the addition of Si- and hydrogen-incorporated tetrahedral amorphous carbon, ta-C:Si:H, films is found to improve the films' thermal stability by raising the temperature at which the hydrogen evolves. This implies that the graphitization tendency observed in our ta-C:H:Si film is most probably due to an increased hydrogen concentration associated with the introduction of TMS in the deposition process.
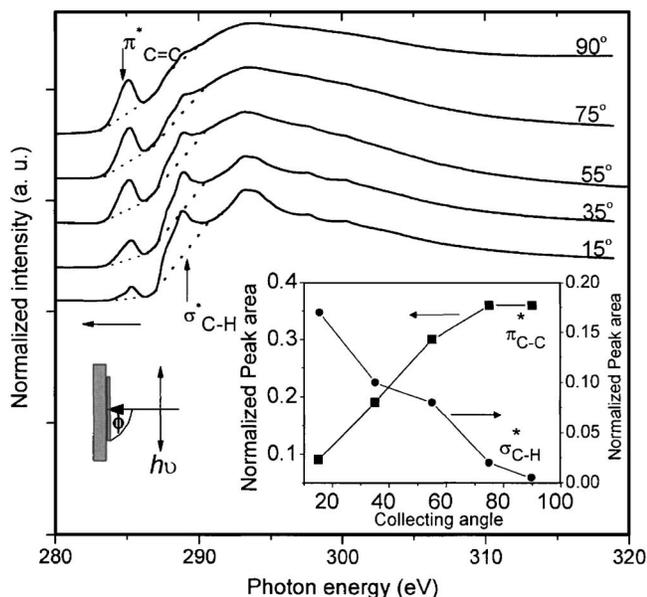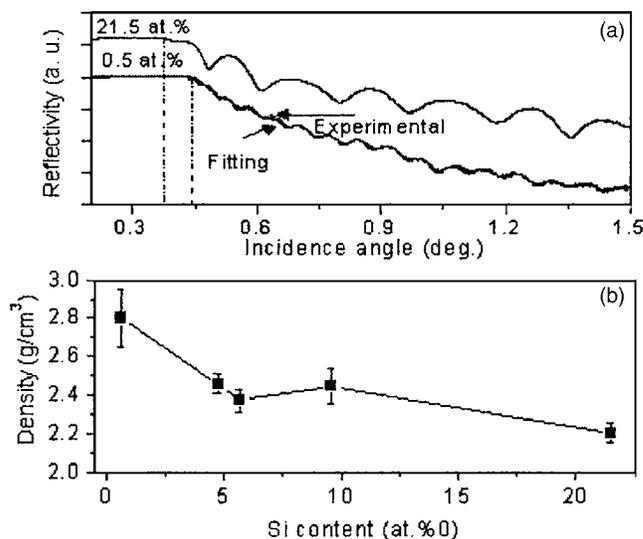
Figure 3 shows the C K-edge NEXAFS spectra of a ta-

FIG. 3. Angular dependence of the normalized NEXAFS spectra of ta-C:H:Si sample (21.5 at. % Si) at the C K edge. The right inset shows the angular dependence of the normalized $\pi_{C=C}^*$ and π_{C-H}^* absorption peaks areas, and the left inset shows a schematic of the incidence angle ϕ.

C:Si:H sample (21.5 at. % Si), collected at different angles ϕ. The angle evolution of $\pi_{C=C}^*$ and σ_{C-H}^* resonance peaks is provided in the right-hand side inset of Fig. 3, while the left-hand side inset shows a schematic of the incident angle ϕ. By increasing ϕ, the intensity of the $\pi_{C=C}^*$ peak improves, while the σ_{C-H}^* intensity strongly decreases. The transitions in NEXAFS spectroscopy, that correspond to $\pi_{C=C}^*$ and σ_{C-H}^* resonance peaks, can be thought of as dipole transitions from C $1s$ core level to the first unoccupied allowed bands (π^* and σ^*) i.e., the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$. The transition matrix elements thus have an angular dependence on the angle made by, for instance, the π^* orbital with respect to the electric-field vector of the incident polarized x rays. Because the synchrotron light is linearly polarized, the intensity of the $\pi_{C=C}^*$ and σ_{C-H}^* resonance peaks is sensitive to the orientation of these orbitals with respect to the polarization vector. Thus, changes in the intensity of resonance peaks, upon rotating the sample in the plane of incidence of the x-ray beam, provide evidence of bond orientation. From Fig. 3, it is clearly obvious that the Si addition has induced structural changes in the amorphous ta-C network. The nanostructure of the surface layer of the ta-C:H:Si film becomes partially oriented to the polarization vector of the incident x-ray beam. However, in contrast to NEXAFS spectra of highly oriented pyrolytic graphite reported in literature,[6] the $\pi_{C=C}^*$ orbitals of the ta-C:Si:H are aligned parallel to the Si substrate. The opposite trends of $\pi_{C=C}^*$ and σ_{C-H}^* intensity peaks with ϕ is a clear indication that $\pi_{C=C}^*$ and a σ_{C-H}^* orbitals are orthogonal to each other. A similar angle-dependent NEXAFS study was performed on ta-C film (figure not shown). The $\pi_{C=C}^*$ and σ_{C-H}^* peaks of the ta-C sample showed a very little change, reflecting that the sp^3 and sp^2 bonds are mainly organized in a short-range ordered network, typical of a-C.

Figure 4(a) shows the XRR data for pure ($\sim$100 nm) and Si-doped ($\sim$50 nm) ta-C films versus scattering angle (2θ), together with a model fit result. Simulation with a six-layer model (including film-substrate interface and film surface layers) gives a very good fit as illustrated in the figure. The position of the critical angle shifted to a lower 2θ value and a double critical angle was developed for the ta-C:Si:H
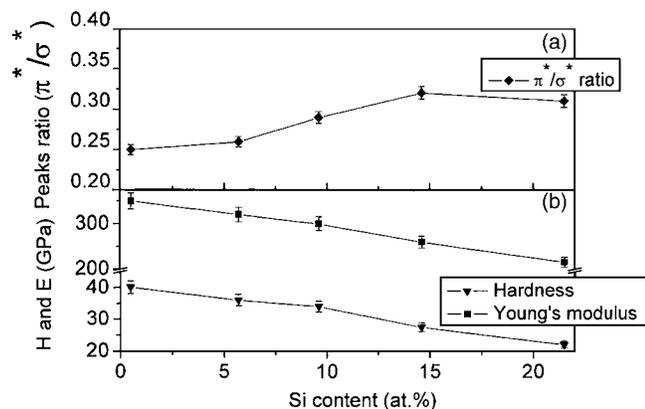
FIG. 5. The evolution of (a) normalized π^*/σ^* peak ratio and (b) Young's modulus and hardness of the ta-C:H:Si films with Si concentration.

film. The shift in the critical angle indicates a decrease in density, while the development of a double-critical angle points out that the ta-C:Si:H film possesses an electron density lower than that of the Si substrate.[7] The best-fit results of XRR curves display a declining trend [see Fig. 4(b)]. The film density decreased from 2.8, for film deposited at zero TMS to a value of 2.2 g cm^3 for film deposited at a TMS flow rate of 40 sccm, indicating the formation of a porous structure. The decline in density of the samples corroborates well with the inferior thermal stability revealed by our *in situ* RTA experiments.

Figure 5 shows that both Young's modulus and hardness progressively decrease as the I_{sp^2}/I_{sp^3} increases, which is in agreement with the observed reduction in density values. This is a typical trend for carbon-related material, in which the exchange between graphitelike sp^2 bonding and diamondlike sp^3 C–C bonding is established. However, this trend is in contrast to the usual observation that the effect of Si-alloying enhances sp^3- and reduces sp^2 bonding. The introduction of TMS in the FCVA deposition chamber could participate in the deterioration in the mechanical properties and/or the mass density of the ta-C:Si:H films in two differ-

ent ways. (i) First, it helps to include hydrogen whose effect is to increase the density of voids and influence the connectivity and hardness of the network.[8] (ii) Second, the kinetic energy of the carbon ions decreases with TMS incorporation due to numerous collisions, thus reducing the density as well as the sp^3 bonding in the growing films. Similar thermalization processes were observed on ta-C films deposited at high partial pressure of nitrogen and argon.[9]

In summary, the comparison of C K-edge NEXAFS spectra of pure and Si-doped ta-C films reveals significant dopant-induced local ordering in $\pi^*_{C=C}$ and σ^*_{C-H} orbitals in a way that, $\pi^*_{C=C}$ orbitals lie parallel to the Si substrate. Also, XRR results provide evidence that the incorporation process has affected the connectivity and hardness of the structural network.

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