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X-ray absorption spectroscopy, simulation and modeling of Si-DLC films

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Amorphous silicon-containing diamond-like carbon (Si-DLC) films were deposited on silicon wafers by Ar^+ Ion Beam Assisted Deposition (IBAD) at various energy conditions. The films were examined with X-ray Absorption Near Edge Structure (XANES) spectroscopy and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy. The Si K-edge X-ray Absorption Spectroscopy (XAS) results indicate that Si-DLC films have an amorphous structure, where each Si atom is coordinated to four carbon atoms or CH_n groups. This short-range order, where a Si atom is surrounded by four C atoms, was found in all Si-DLC films. The XANES spectra do not indicate Si coordination to oxygen atoms or phenyl rings, which are present in the precursor material. A structural model of Si-DLC is proposed based on XAS findings. Simulated X-ray absorption spectra of the model produced by FEFF8 show a good resemblance to the experimental data.

1. Introduction

Diamond-like carbon (DLC) and silicon-containing DLC (Si-DLC) films in particular, have been extensively studied over the past several years due to their significant importance for tribological applications [1–4]. Also, Si-DLC films possess the potential to improve wear performance at higher temperatures and in humid environments [5]. Recent studies have shown that incorporation of Si in DLC films has been found to promote the diamond-like character of the film, and decrease its hardness and coefficient of friction [4]. At present, the role of Si in DLC is not well understood. In this study, Si-DLC coatings were prepared by the ion beam-assisted deposition (IBAD) process on Si substrates, using an Ar^+ ion beam at various energy levels and tetramethyl-tetraphenyl-trisiloxane as a precursor material. The purpose of the present work was to probe the local environment of the Si atoms in Si-DLC coatings using Si K-edge X-ray Absorption Spectroscopy (XAS) and provide additional insight on the role of Si in the DLC structure.

2. Experimental

In this study, Si-DLC coatings were prepared by the IBAD process on Si (111) wafers, using an Ar^+ ion beam and tetramethyl-tetraphenyl-trisiloxane (704 Dow-Corning diffusion pump oil) as a precursor material. The Ar^+ beam was operated at 40 and 50 keV and various current densities. Table I presents the various deposition conditions. Details of the deposition process are described elsewhere [2–4].

2.1. Wavelength-dispersive spectroscopy (WDS)

WDS was used to measure the stoichiometry of the films. It was performed on a Jeol Superprobe 733, with a beam current of 10 nA, an accelerating voltage of 15 keV, and a beam size of 20 μm. All films exhibited similar compositions with an average of (in atomic percent): 10% Si, 80% C, 6% O, 4% Ar. This does not include hydrogen, which is also present in the films but is not detectable by this method.

2.2. XAS analysis

Si K-edge XAS spectra were recorded at the J. Bennet Johnston, Sr., Center for Advanced Microstructures and Devices (CAMD), Louisiana State University. Data were collected using bending magnet radiation at the DCM1 beamline, where the X-ray beam was monochromatized with a fixed exit double crystal monochromator, operating with InSb crystals providing an energy resolution of approximately 0.8 eV at 2000 eV. The incident monochromatic X-ray intensity (I_o) was monitored with an ionization chamber and

TABLE I Processing conditions (Ar^+ energy and current density) for deposition of Si-DLC films

Si-DLC	Film 1	Film 2	Film 3	Film 4	Film 5
Processing conditions	50 keV, 163 μA cm^{-2}	50 keV, 85 μA cm^{-2}	50 keV, 143 μA cm^{-2}	40 keV, 100 μA cm^{-2}	40 keV, 195 μA cm^{-2}

XAFS spectra were recorded in total electron yield (TEY) mode with a Lytle apparatus, with a continuous helium flow through the detector chambers [6]. EXAFS spectra were recorded over an energy range of 1809–2539 eV with 1 eV steps; XANES spectra were recorded from 1809–1989 eV with 0.3 eV steps in the near edge region. The TEY and I_0 detector signals were divided (TEY/I_0) to yield the raw spectral data.

XANES data were fitted with a linear pre-edge for background removal and normalized to the 1920–1980 eV post-edge regions of the spectra using the WinXAS software package [7]. The EXAFS data were extracted and analyzed utilizing the UWXAFS software package [8]. Background removal and normalization were performed using the AUTOBK routine in the UWXAFS package. E_0 was set at the first inflection point of the Si spectrum, and the extracted EXAFS signal was Fourier transformed over the region of 4.0 Å^{-1} to 9.5 Å^{-1}, using a Hanning window function. Refined structural parameters were obtained from nonlinear least square fitting in R-space over a range of 0.9 Å to 2.1 Å, encompassing the first peak representing Si... C in the single scattering approximation. Theoretical phase and amplitude functions were calculated using FEFF8, a computer program for *ab initio* calculation of EXAFS and XANES spectra using multiple-scattering theory [9]. The amplitude reduction factor $S_0{}^2$ was determined by fitting the EXAFS data of the SiC powder standard, yielding a value of 0.791.

Spectra of a number of organic and inorganic Si compounds were taken as structural references.

3. Results and discussion

3.1. XANES

Fig. 1 shows normalized XANES spectra of the five Si-DLC films (Table I). All samples in this study demonstrated very similar X-ray absorption spectra, with the white line consisting of two peaks and a large, broad resonance at about 15 eV above the absorption edge.

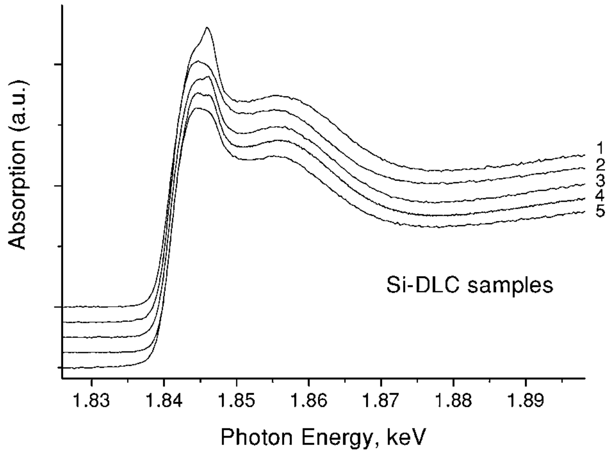

Figure 1 XANES spectra of Si-DLC films deposited under the conditions shown in Table I.

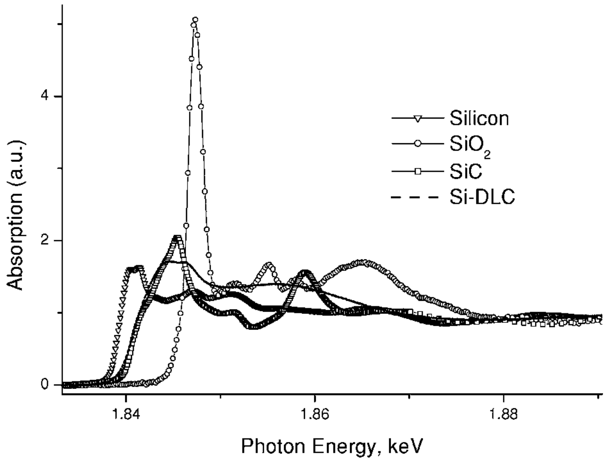

Figure 2 XANES spectra of Si-DLC and reference materials: Si, SiC, and SiO_2.

Fig. 2 shows XANES spectra of a Si-DLC sample and several reference materials: Si, SiC, and SiO_2. Based on the chemical composition of the precursor, the Si atoms in these films may be expected to have Si, C, H, and/or O as near neighbors. The chemical environment around the absorbing atom will determine the white line intensity and the position of the absorption edge, E_0, which is usually defined as the first inflection point in the absorption spectrum. As can be seen in Fig. 2, E_0 shifts towards higher energy with increasing positive charge on the absorber, and increasing electronegativity of the ligand causes an increase in the white line amplitude. The edge position ($E_0 \sim 1841$ eV) and the amplitude of the white line in Si-DLC samples are somewhat similar to those of SiC. This indicates that formation of clusters composed primarily of Si atoms does not occur; instead, Si atoms are incorporated in the carbon network. Si atoms are also unlikely to have O nearest neighbors, which would cause a corresponding E_0 shift and an increased white line amplitude. This effect can be observed in the spectrum of the precursor material, which is shown in Fig. 3 with the Si-DLC and SiC spectra. Another interesting feature of the precursor spectrum is the pre-edge resonance at about 1842 eV.

The Si atoms in tetramethyl-tetraphenyl-trisiloxane [$(CH_3)_4(C_6H_5)_4O_2Si_3$] are coordinated to methyl groups, phenyl groups, and O atoms. We suggest that the 1842 eV feature appears due to the presence of phenyl rings. The spectrum of octamethyltrisiloxane, which has essentially the same structure but without the phenyl rings, does not have this feature, while in the spectrum of phenylsilane [$(C_6H_5)H_3Si$], this energy corresponds to the white line maximum (Fig. 4). As can be seen in Fig. 3, the pre-edge of the Si-DLC spectrum resembles that of SiC and does not have any pronounced features at that energy.

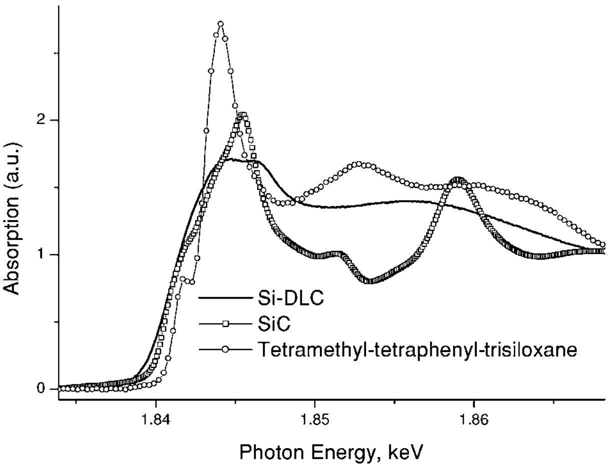

Figure 3 XANES spectra of the precursor material, Si-DLC and SiC.

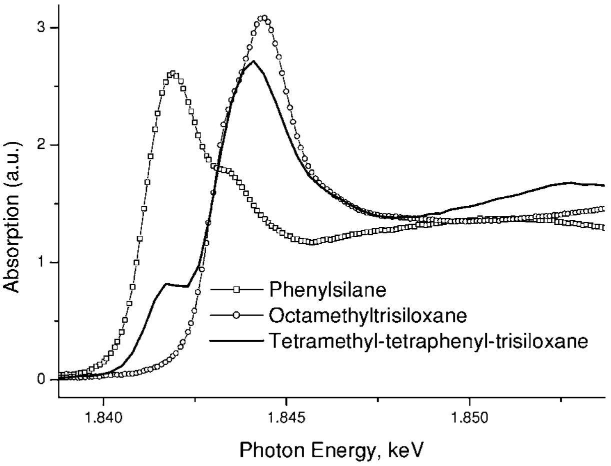

Figure 4 Origin of the 1842 eV feature: possibly due to the presence of phenyl rings.

This indicates that the phenyl rings, present in the precursor material, very likely become dissociated by ion bombardment, and similar aromatic structures are not formed in the films during the deposition process.

Therefore, based on XANES fingerprinting, we expect the first coordination sphere of Si in the Si-DLC films to consist of approximately four C atoms, as in SiC. It is interesting to note that some of the XANES spectra for a-Si_{1-x} C_x : H samples prepared by plasma-enhanced chemical vapor deposition (PECVD) technique, reported by Mastelaro, *et al.* [10], were very similar to the spectra of Si-DLC films observed in this study. These spectra also feature the broadened white line consisting of two peaks and a broad resonance at about 15 eV above the absorption edge. The resemblance of the spectral features suggests that these samples may have similar atomic structures as well. It should be mentioned that the sample stoichiometries estimated by Mastelaro, *et al.* based on the optical gap values were significantly different from those measured for our samples by WDS. These measurements, combined with XANES fingerprinting, EXAFS fitting and theoretical modeling, allow us to propose a different interpretation of these spectra, as discussed elsewhere in this paper.

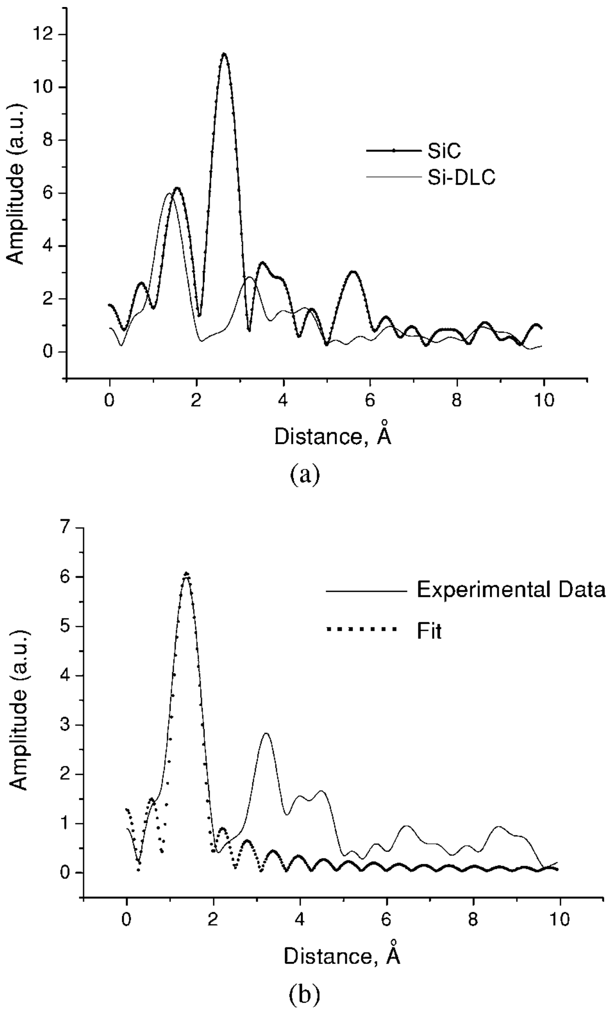

Figure 5 (a) Fourier transformed EXAFS data of SiC and Si-DLC; (b) EXAFS-FT and fitting results for Si-DLC.

3.2. EXAFS

Fig. 5a presents the Fourier transforms of the EXAFS data of c-SiC and a representative Si-DLC sample. Only the first-shell signal can be seen clearly in the radial distribution function of Si-DLC, with the amplitude close to that of the first shell Si—C interaction in SiC. This indicates the presence of short-range order in the films, at least at the level of the first coordination shell. This is in agreement with previous electron diffraction studies that showed that these films are mainly amorphous (no long-range order) [4]. In an effort to obtain the structural parameters, fitting of the EXAFS data with one-shell, single-scattering model was performed over $r = 0.9$–2.1 Å, $k = 4.0$–9.5 Å^{-1}. The best fits were obtained when only C atoms were present in the first shell, producing the first-shell coordination number of $n_C = 4.1 \pm 0.55$, and the Si—C distance $r_{\text{Si-C}} = 1.81 \pm 0.02$ Å. Fitting results are shown in Fig. 5b. Attempts to include Si or O atoms in the first coordination shell of Si resulted in significant reduction of the quality of fit parameters.

Kaloyeros, *et al.* [11] reported a decrease in the coordination number of carbon caused by an addition of hydrogen, while the coordination number of silicon remains unchanged. This indicates that hydrogen atoms in a-SiC : H samples bond mainly to carbon.

Since the H atoms cannot be directly detected by EXAFS due to their small backscattering amplitude, their presence in the Si-DLC films could only be seen as an apparent decrease of the coordination numbers as measured by EXAFS. However, our XAS results do not indicate any reduction in the coordination number of Si, which supports the conclusion that hydrogen is bonded primarily to carbon.

This is consistent with our model of "amorphous hydrogenated SiC" described in the next section, where most of the Si atoms are coordinated to four C atoms, while the first coordination shell of the C atoms consists of H, C, and Si atoms.

3.3. FEFF8 simulations and modeling

FEFF8 modeling of an amorphous SiC species with C tetrahedrally coordinated to Si resulted in simulated XANES spectra very similar to the experimental spectra of Si-DLC (Fig. 6). Based on XAS results, the first coordination shell of the central atom (Si) is a tetrahedron of C atoms, which can be placed in the SiC lattice positions, with the Si—C distance adjusted according to the EXAFS fitting results. A simulated absorption spectrum with only one coordination shell does not show a good resemblance to the experimental spectra. A second shell was constructed by placing C and Si atoms in the crystallographic sites of the second shell of the SiC lattice, with the proper Si—C and C—C distances. Models with only Si or only C atoms in the second shell failed to produce a good match to the experimental spectra. A series of simulations with different Si/C ratios in the second shell was calculated, starting from both Si-only and C-only models and gradually adding atoms of the second element to see how it affected the resulting spectrum. The best matches were produced by using 1–3 Si and 3–5 C atoms in the second shell. This coordination number is significantly lower than in SiC, which has 12 Si atoms in this shell. This apparent reduction of C (1st shell atoms) coordination number can be caused by two phenomena: the presence of H nearest neighbors, not detectable by X-ray techniques, and the fact that some C atoms are sp^2 hybridized. Thus, the "building block" used to construct the model is: (1) central Si atom (absorber), (2) first shell—4 C atoms, (3) second shell—4 C and 2 Si atoms. Several additional atoms (mostly C) were used beyond the second shell (3rd shell and greater), in order to produce the same short-range (2 coordination spheres) environment for all Si atoms in this cluster as for the central atom, to produce the correct stoichiometry, and to improve the connectivity of the resulting network. Then, the ATOMS program was utilized to fill the space by repeating this cluster periodically, by setting it to be a unit cell of a monoclinic (space group P1) lattice. The simulated spectrum is shown in Fig. 6 and a fragment of the resulting "amorphous" network is shown in Fig. 7.

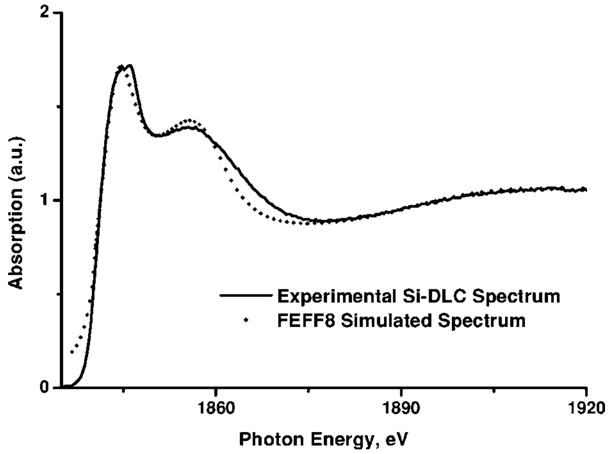

Figure 6 FEFF8-simulated and experimental XANES spectra.

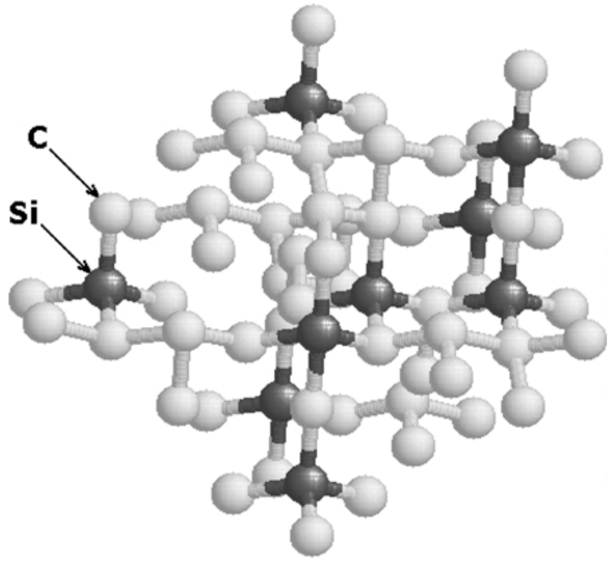

Figure 7 Model of Si-DLC structure.

4. Summary

The present results show that the Si-DLC films produced by Ion Beam Assisted Deposition have an amorphous structure, in which the local environment of the Si atoms was quite different from that in the precursor material. The first coordination shell of the Si atoms was found to consist of four C atoms, and the first coordination shell of the C atoms consisted of H, C, and Si atoms. Based on XANES and EXAFS results the authors suggested a model of atomic structure of Si-DLC. This model was used to produce FEFF8 simulated XANES spectra, which were very similar to the experimental data.

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