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Wavelength-dependent Raman scattering of hydrogenated amorphous silicon carbon with red, green, and blue light excitation

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This study presents results of wavelength-dependent Raman scattering from amorphous silicon carbon (a-Si:C:H). The a-Si:C:H films were produced by radio-frequency plasma-enhanced chemical vapor deposition. Prior results with amorphous carbon indicate that laser excitation selectively probes clusters with differing sizes. Our measurements with a-Si:C:H indicate that when using red (632.8 nm), green (514.5 nm), and blue (488.0 nm) excitation, the Raman D and G peaks shift to higher wave numbers as the excitation energy increases. The higher frequency is associated with smaller clusters that are preferentially excited with higher photon energy. It appears that photoluminescence occurs due to radiative recombination from intracluster transitions in Si-alloyed sp^2 -bonded carbon clusters.

I. INTRODUCTION

Wavelength-dependent Raman scattering, which takes advantage of the resonant effect, is an extremely powerful technique to analyze nanometer-sized clusters embedded in a matrix. It exploits the band-gap difference between a particle and the matrix so that nanometer-scale particles can be selectively probed. The resonance condition is achieved when the excitation energy of the laser is close to the energy of an electronic transition, resulting in a significant increase in the Raman scattering cross section.¹ When the laser excitation energy is tuned, the resonant effect allows one to selectively probe the vibrational frequency of the nanoparticles, which have different excited-state energy levels. Besides carbon materials, wavelength-dependent Raman scattering has been used by de Paula *et al.* to study size effects on the phonon spectrum of CdTe-doped glasses.²

It has been conjectured that hydrogenated amorphous silicon carbon (a-Si:C:H) contains nanoscopic sp^2 -bonded clusters of fused aromatic rings, which are

embedded in a highly sp^3 -bonded matrix.³ A resonant Raman scattering effect from amorphous carbon (a-C) has been observed by Wagner *et al.*^{4,5} It was shown that the a-C Raman peak shifted to higher frequency with increasing excitation photon energy. They proposed that smaller clusters possess higher vibrational frequencies than larger clusters by making an analogy with transpolyacetylene, where the vibrational frequency changes as a function of the conjugation length of polymer chains.⁶ A similar effect was reported by Yoshikawa *et al.*⁷ and Tamor *et al.*⁸ However, no research has been devoted to wavelength-dependent Raman scattering of amorphous silicon carbon materials. Therefore, in this letter, we present the excitation energy-dependent resonant Raman scattering of a-Si:C:H and provide new insight to understand this phenomena exhibited by carbon materials.

II. EXPERIMENTAL

The a-Si:C:H thin films were deposited onto Si(100) using a capacitively coupled 13.56-MHz radio-frequency plasma-enhanced chemical vapor deposition (rf-PECVD) system. Tetramethylsilane [$\text{Si}(\text{CH}_3)_4$] was used as a precursor. The rf power was 200 W, and the substrate bias was -300 V. The pressure of the chamber was 50 mtorr.

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The total concentration of hydrogen that is bonded to C and Si is $5.3 \times 10^{22} \text{ cm}^{-3}$, which was determined with an infrared absorption study. The films were analyzed by x-ray diffraction, Auger electron spectroscopy, atomic force microscopy, micro-Raman scattering, optical transmission, and photoluminescence (PL) spectroscopy. Micro-Raman spectroscopy and visible PL spectroscopy were carried out at room temperature using backscattering geometry with the 514.5 nm (2.41 eV) and 488.0 nm (2.54 eV) lines of an Ar ion laser using an ISA U-1000 (Jobin Yvon Inc., Edison, NJ) scanning double monochromator. Similar measurements were obtained using the 632.8 nm (1.96 eV) line of a HeNe laser and a Dilor LabRam micro-Raman spectrometer. The Fourier transform infrared spectroscopy was performed using a BOMEM FTIR (ABB Bomem Inc., Quebec, Canada) spectrometer. PL spectra were also obtained with the 305.0 nm (4.07 eV) line of an Ar ion laser and a 0.64 m spectrometer.

III. RESULTS AND DISCUSSION

X-ray diffraction analysis indicated that the material investigated is amorphous. The composition of the film, determined from Auger electron spectroscopy, is approximately $\text{Si}_{0.33}\text{C}_{0.67}$. Atomic force microscopic analysis ($2 \times 2 \mu\text{m}$) found a root mean square surface roughness of approximately 1.4 \AA , which indicates that the film surface is extremely smooth.

The Raman spectrum of carbon-rich a-Si:C:H can be analyzed relative to that of a-C:H on the basis of the proposed structures of amorphous silicon carbon as sp^2 -bonded a-Si:C:H clusters and an sp^3 -bonded a-Si:C:H matrix. The typical Raman spectrum of amorphous carbon consists of two broad bands, a D band (D for disordered) at approximately 1350 cm^{-1} and a G band (G for graphite) at about 1580 cm^{-1} . The first-order Raman spectrum of single-crystal graphite displays two modes, both of E_{2g} symmetry: a low-frequency $E_{2g}^{(1)}$ mode (42 cm^{-1}) and a high-frequency $E_{2g}^{(2)}$ mode (1581 cm^{-1}).⁹ The high-frequency $E_{2g}^{(2)}$ mode is considered to be the origin of the G peak. The D peak is attributed to a disorder-induced A_{1g} mode at the \mathbf{K} point in the Brillouin zone of graphite.¹⁰ This mode is observed due to the relaxation of the wave vector selection rule upon loss of long-range translational symmetry.¹⁰ When a material is amorphized, disorder in bond-angle is produced, resulting in a loss of the crystal symmetry and a relaxation of wave vector conservation.⁹

Figure 1 shows the wavelength-dependent Raman spectra of a-Si:C:H excited with 632.8 nm (1.96 eV), 514.5 nm (2.41 eV), and 488.0 nm (2.54 eV). Two sets of functions were used to fit the Raman spectra. First, both the D and G peaks were fit with two Gaussians and a linear background. Second, the spectrum was fit

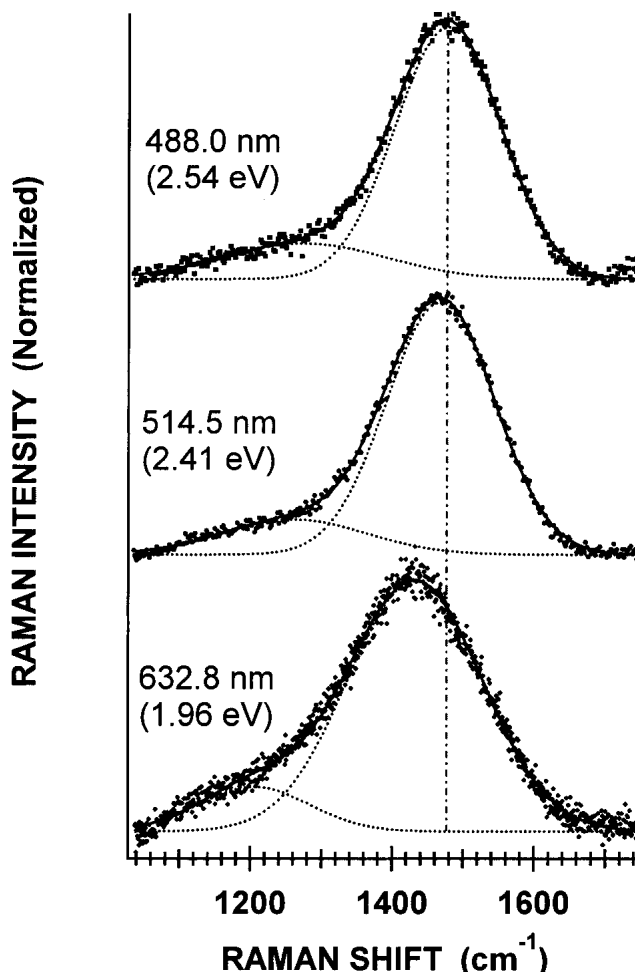


FIG. 1. Wavelength-dependent Raman spectra of amorphous silicon carbon (approximately $\text{Si}_{0.33}\text{C}_{0.67}$) excited with 632.8 nm (1.96 eV), 514.5 nm (2.41 eV), and 488.0 nm (2.54 eV).

with a Lorentzian (D peak), a Breit-Wigner-Fano (BWF) (G peak) line shape, and a linear background. The Lorentzian-BWF has previously been used for line-shape analysis of the Raman spectra of disordered carbon.^{11,12} The BWF function is expressed as

$$I(\omega) = \frac{I_0[1 + 2(\omega - \omega_0)/Q\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2}, \quad (1)$$

where I_0 is the intensity of the Raman peak, ω_0 the frequency of the mode, Q the BWF coupling coefficient, and Γ the full width at half-maximum (FWHM) of the peak. As Q^{-1} approaches 0, the line shape approaches that of a Lorentzian. The BWF line shape is known to occur in Raman spectra due to the coupling between discrete vibrational modes and a Raman active continuum.¹³ The result of the fitting are summarized and plotted in Figs. 2 and 3.

As is displayed in Fig. 2, both the D and G peak positions shift to higher wave number as the excitation photon energy of the laser increases. Note that it was

difficult to accurately determine the D peak (L + BWF) position since the D peak (L + BWF) is only a small portion of the shoulder of the spectrum and most of the high-frequency portion of the spectrum was fit by the asymmetric BWF G peak. This interaction shifts the Lorentzian D peak to an apparent lower wave number. A similar observation was made by Ferrari *et al.*¹⁴

The upshift of the D and G peaks may be explained in terms of selective excitation of sp^2 -bonded clusters with different band gap via the resonance effect. It appears that our film is composed of a broad distribution of different sized carbon clusters, and the different cluster sizes can be probed by changing excitation energy. The results suggest that smaller clusters exhibit a higher vibrational phonon frequency than larger clusters. This is

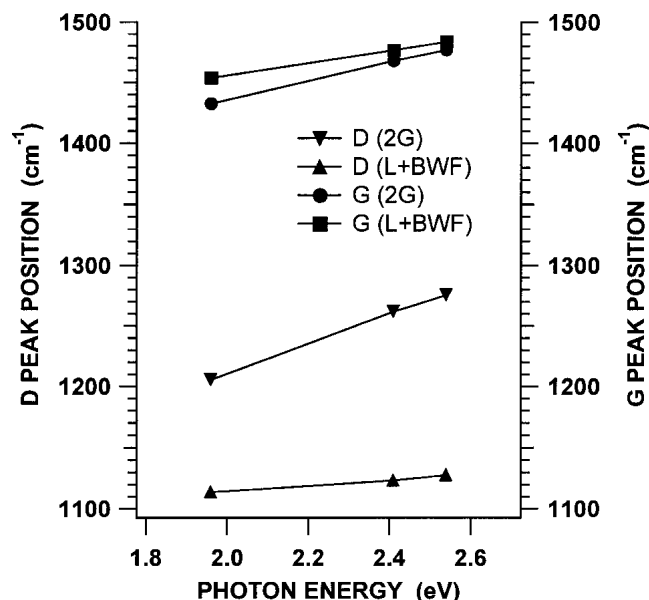


FIG. 2. Position of the Raman D and G peaks determined from a fit using two Gaussians and a Lorentzian + BWF.

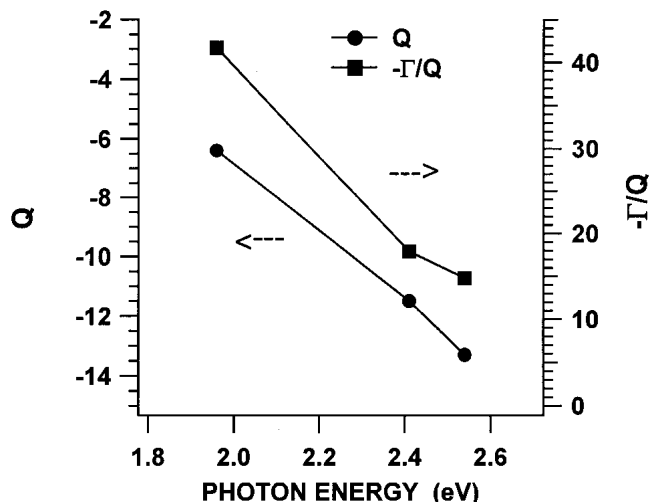


FIG. 3. BWF coupling coefficient (Q) and coupling parameter ($-\Gamma/Q$) as deduced from the fits.

plausible since it has been proposed that sp^2 sites are under tensile stress, while sp^3 sites are under compressive stress.¹⁵ From a prior Raman study, Bergman *et al.* suggested that the presence of an sp^2 -bonded graphitic phase promotes compressive stress in a diamond matrix and the sp^3 -diamond matrix becomes under increased compressive stress as the graphitic phase concentration increases.¹⁶ As the size of the sp^2 clusters in the a-Si:C:H increases, the sp^3 -bonded matrix will be under more compressive stress. To relieve internal strain by balancing the local compressive and tensile stress, the sp^2 clusters will be under increased tensile stress. Therefore, the sp^2 -related Raman frequencies will shift to a higher wave number as the excitation energy increases since the higher photon energy will probe smaller clusters. A similar size-dependent effect for Raman scattering from semiconductor nanocrystals embedded in glass has been explained in terms of strain.¹⁷

The shift in the D and G peaks as a function of excitation wavelength can be explained from a different perspective. Smaller clusters may contain fewer Si atoms than larger clusters, which increases the vibrational frequencies of the smaller clusters. It is known that the positions of both the D and G peaks of a-C:H shift to lower wave numbers as Si is incorporated into the film.¹⁸ It was suggested that the decrease of the Raman frequency upon Si addition occurs because the Si-C bond is weaker than the C-C bond and Si atoms are more massive than C atoms. Carbon atoms in the sp^2 -bonded clusters may be replaced by silicon atoms, reducing the vibrational frequency of the graphitic ring.¹⁹ Therefore, incorporation of Si into C clusters will reduce the phonon vibrational frequency, shifting both D and G peaks to a lower wave number. Note that D peak exhibits dispersion characteristics even in crystalline graphite.^{20,21}

The BWF coupling parameter ($-\Gamma/Q$) has been used to estimate the in-plane graphitic order in ion-beam-irradiated glassy carbon²² and ion-implanted graphite.²³ As $-\Gamma/Q$ goes to 0, the in-plane graphitic order increases. From Fig. 3, we can see that $-\Gamma/Q$ is reduced as the excitation photon energy increases. Therefore, it may be suggested that smaller clusters are more ordered. However, further investigation is required to unambiguously address the question of whether we can extend this interpretation on the basis of samples with different "average" cluster sizes to the analysis of dispersion of the D and G peaks found in the same sample. Determination of a radial distribution function from x-ray scattering or electron diffraction may provide useful insight to elucidate this issue.

Figure 4 shows PL spectra of a-Si:C:H with 514.5 nm (green) and 305.0 nm ultraviolet (UV) excitation. A shift in the PL peak energy was observed between the UV and visible light excitation. Similar shifts have been attributed to the fact that the material is composed of various

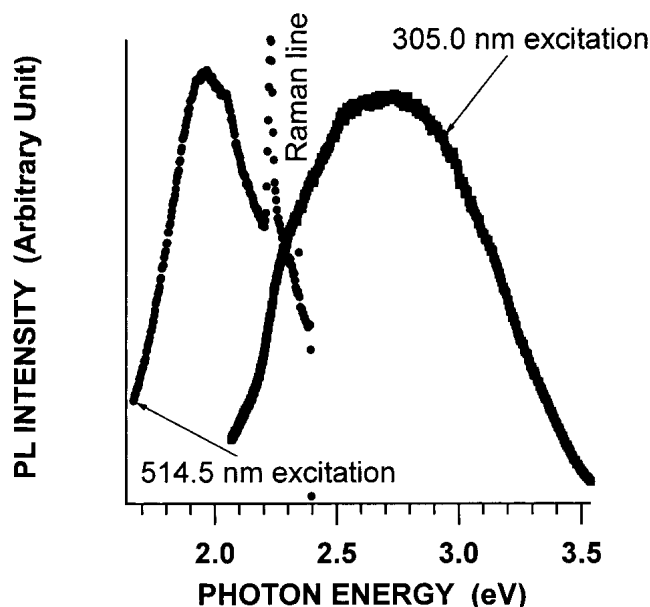


FIG 4. PL spectra obtained using 514.5 and 305.0 nm.

sized sp^2 clusters with different band gaps, which is consistent with the model presented by Robertson *et al.*²⁴ The FWHM of the PL with 514.5-nm excitation was smaller than that with UV excitation. Following the model of cluster excitation, this means that higher energy photons can excite PL in a larger number of clusters with varying size. This result is consistent with that found by Rusli *et al.* in hydrogenated amorphous carbon (a-C:H).²⁵ According to their results, PL peak energy and the FWHM of the peak increases with increasing excitation energy.

IV. CONCLUSION

In conclusion, wavelength-dependent Raman scattering was presented for a-Si:C:H. Models have suggested that red, green, and blue laser excitation selectively probes clusters with differing sizes. The Raman D and G peaks shift to a higher wave number as the excitation energy increases. On the basis of the cluster excitation model, the higher photon energy will probe smaller clusters, and the results indicate a higher vibrational frequency of the smaller clusters. It appears that PL occurs due to radiative recombination from intracluster transitions in Si-alloyed sp^2 -bonded carbon clusters. We suggest that these effects may contribute to this observation: (i) The smaller clusters may be under compressive strain. (ii) They may be carbon rich. (iii) They may be more

ordered. The PL peak also shifts to higher energy with high-energy excitation, suggesting that smaller clusters may have a larger band gap.

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