Use of Raman spectroscopy in the characterization of soft x-ray multilayer reflectors

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ABSTRACT

Laser Raman spectroscopy has been found to be useful for characterizing amorphous semiconductor multilayers especially the interfaces of multilayers. We have extended this technique to the characterization of W/C multilayers used in soft x-ray optics and ultrathin sputtered carbon films. Unlike the multilayers previously studied which contained only semiconductors and dielectrics, these are semiconductor/metal multilayers. The dominate Raman feature is due to a-C and consists of a broad peak at about 1580 cm^{-1} (G-peak) and a shoulder at about 1400 cm^{-1} (D-peak). This was deconvoluted with Gaussians to yield two peaks (one at 1570 cm^{-1} and the other at 1420 cm^{-1}). Among the multilayer samples peak positions and relative magnitudes changed little. The intensity ratio of the D-peak to G-peak was much larger for multilayer sample, however , than for the single layer pair samples. This may due to different forms (amorphous or crystalline) of tungsten layer in the samples and indicate the differences in the structure of carbon layers and/or bonding structure at interfaces.

1. INTRODUCTION

The Raman spectra of amorphous carbon in multilayers has not been previously reported.The Raman spectra of bulk graphite,[1,2] glassy carbon and thin film a-C[3]is, however, well known. There are two main bands observed. One is related to the graphite E_{2g} mode (G-line) at $\sim$1580 cm^{-1} and the other, which is due to disorder (D-line), is at $\sim$1390 cm^{-1}.[2,4] The information from these two lines, such as central frequencies, the intensity ratio and line widths are useful in the study of the amorphous carbon structure.

In this paper we report on Raman spectrum of W/C multilayers and ultrathin carbon layers on tungsten. Bulk tungsten is opaque to the visible light. In the multilayer case tungsten is in the form of an ultrathin film, only a few nanometers thick. It is possible, therefore, for the laser light to penetrate several layers of tungsten and excite the Raman signal of buried carbon. We find that the position of the peaks is relatively constant and the ratio of their magnitudes is rather constant in all of the multilayer samples. The observed Raman data shows that the intensity ratio of the two lines is relatively larger for multilayers than those for the thick carbon film and thin carbon film on thick tungsten. A possible reason for this phenomena are discussed.

2. SAMPLE PREPARATION

All samples were prepared by DC magnetron sputtering. The multilayer samples were similar to those used as mirrors in soft x-ray optics. They consist of two sputtered materials carbon and tungsten, arranged alternately in layers of the thickness d_C and d_W respectively so that the

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periodicity of the structure was $d=d_C+d_W$. The substrates were Si wafers and both the top and bottom layers were carbon. There were 20 pairs of layers in each sample. In the first set of samples d_W was kept constant, at a nominal thickness of 20Å and d_C ranged from 10Å to 80Å. A supplementary set of two multilayer samples also with d_W=20Å (nominal) were prepared later.

The d-spacing of the multilayer samples were determined by using low angle x-ray diffraction. By comparing the relative intensity ratios of the peaks of the various diffraction orders with those from computer generated diffraction patterns it was possible to estimate the values of d_C and d_W for the samples.

For comparison another set of samples consisting of a singe carbon layer on top of a thick sputtered tungsten film ($\sim$ 450Å) on a Si substrate was prepared. The thickness of the carbon layer in this set ranged from 20Å to 120Å. We termed these the W/C single layer pair samples.

3. EXPERIMENTAL AND DATA FITTING

The Raman setup is shown schematically in Fig.1. An Ar ion laser (LEXEL 96) was used as the excitation source for the Raman spectrum. The 488-nm line at a power of about 400 mw was used in most measurements. The laser beam was focused on the sample surface with an angle of about 70° to the surface normal by a cylindrical lens.

The collection lenses, normal to the sample's surface collected and focused the scattered light on the entrance slit of a SPEX 1877 Triplemate spectrometer. The spectrometer consists of a modified Czerny-Turner zero-dispersion double spectrometer as the filter stage and a modified Czerny-Turner spectrograph. The dispersion element used in the spectrograph stage was a 1800 gr/mm holographic grating with 0.92 nm/mm dispersion. The spectral coverage was set at about 18 cm^{-1}.

At the exit slit, a photomultiplier (EMI 7981B) and photon counting electronics were used to convert the light signal into the analog electrical signal which was recorded on a strip chart recorder or stored digitally using a HP-216 computer controlling a TransEra-MDAS-7000 data acquisition system. The digital system (via signal averaging) was essential for signal enhancement for samples containing the smallest amounts of carbon. The computer was also used to control the wavelength drive for the monochrometer.

The wavelength-dependent intensity response of the whole Raman spectrum collecting system, collection lenses, spectrometer and photomultiplier were calibrated by using a 45-W tungsten-halogen lamp (Optronic Laboratories Standards).

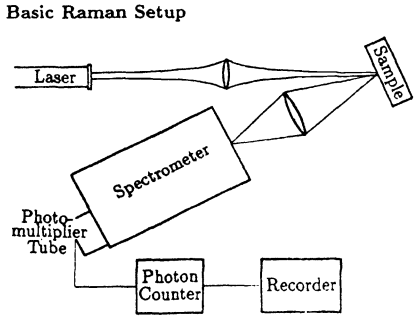


Fig. 1.

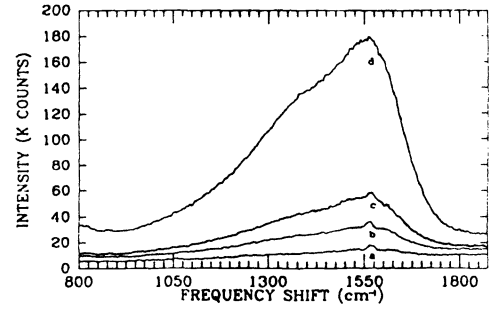


Fig. 2. Raman spectra of W/C multilayers. d_C in each layer is 10Å, 20Å, 40Å and 80Å for the curves labeled a to d.

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The carbon in the samples gave the only significant Raman signal in the 800-1800 cm^{-1} region of frequency shift. The tungsten in the multilayer acts primarily as an attenuator to the Raman signal from the carbon layers underneath.

Fig.2 shows the observed Raman spectrum of four W/C multilayers. Since the absorption coefficient of tungsten is much greater than that of carbon the depth which the laser light can penetrate is mainly decided by the thickness of the tungsten. Thus the intensity of the carbon Raman signal increases when d_C increase. In each case approximately the same number of interfaces is sampled. At the present, however, we have not been able to identify the Raman spectrum characteristic of tungsten carbide.

The Raman spectra between 900 and 1800 cm^{-1} is dominated by two broad features, a peak, which is associated with the carbon G-line at about 1580 cm^{-1} and a shoulder, associated with the carbon D-line at about 1390 cm^{-1}.[5,6] The appearance of the Raman spectra depends on the relative magnitude of the two features and to a lesser extent on any changes in relative positions and widths. To better understand the relationship between the features the observed Raman spectrum for carbon films in this region is frequently treated as the envelope of a D-peak and a G-peak and is deconvoluted as such.[5,6] In our curve fitting procedure the envelope was decomposited into two Gaussian shaped lines and a baseline. Various fits to the data are possible depending on how the base line is chosen and how the noisy traces are smoothed. This allowed us to estimate the accuracy to which the parameters can be fitted to the data. Fig.3 is a typical fitting example. The fitting is good except sometimes around 1400 cm^{-1}. The deviation below 1000 cm^{-1} is due to other carbon Raman peaks at lower frequencies and they are not considered in this study further.

4. RESULTS

Fig.4 shows the change in the G and D peak central frequency as a function of d_C. As the increasing of d_C from about 10Å to 120Å neither the G or D peak central frequency shifts significantly. Generally the error bars are larger for samples which produce a weak Raman spectrum such as the 10Å C/20Å W multilayer. However, for samples containing a-C layers thicker than 10Å the position of the G-line could be obtained to good accuracy $\pm$3-5 cm^{-1}. The position of the D-peak central frequency, at about 1420 cm^{-1}, is determined with less precision than that of G-peak, but within the accuracy of the measurements does not change with thickness.

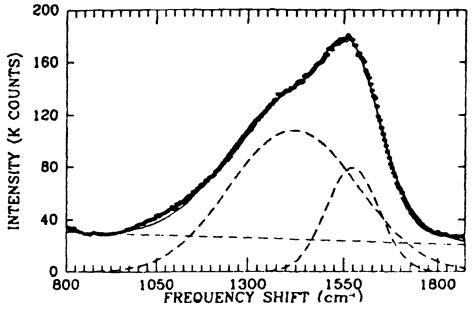


Fig. 3. Raman spectrum of a W/C multilayer fitted by two Gaussians. The one centered at about 1420 cm^{-1} is D-peak and at about 1570 cm^{-1} is G-peak.

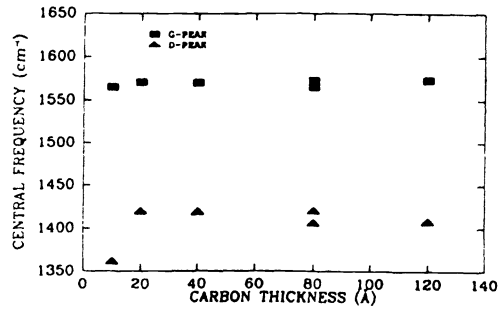


Fig.4. Central frequencies of D-peak and G-peak vs. carbon layer thickness for multilayers.

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Fig.5 gives the relationship between the intensity ratio of D-peak to G-peak and d_C. This ratio is relatively sensitive to fitting for samples which contained the least amount of carbon, namely those with d_C equal to 5Å and 10Å. Beyond 10Å, however, within the accuracy of the fitting the ratio is a constant 3.5 for the W/C multilayer samples.

The Raman spectra of a W/C single layer pair sample (80Å C on 450Å W) is shown in Fig. 6. For comparison the spectrum of a multilayer sample is also plotted. Its maximum intensity is scaled to equal that of the single layer to aid in comparison. The single layer pair sample's spectra

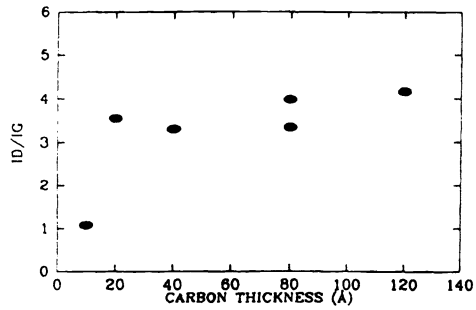


Fig. 5. The intensity ratio of D-peak to G-peak for multilayers.

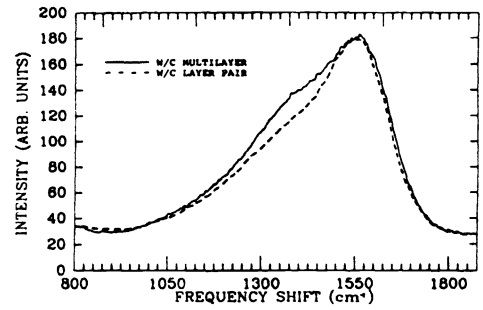


Fig. 6. Comparision of the Raman spectra of multilayer with that of layer pair. Note the difference at about 1400 cm^{-1}.

differs from the multilayer samples in that the magnitude of the feature at about 1580 cm^{-1} is much larger. The computed intensity ratio I_D/I_G of the layer pair samples is much less than that of multilayer.

For comparison with the multilayer and layer pair samples the Raman spectra of a single sputtered carbon film (~2000Å thick) on a Si substrate was measured. The intensity ratio I_D/I_G is lower than that of any multilayer sample but comparable to that of ultrathin carbon in the layer pair samples.

5. DISCUSSION

The most marked differences in Raman spectra between various samples is the relatively high magnitude of the shoulder associated with D feature at about 1390 cm^{-1} in the multilayer samples. It has frequently been found to be the case for elemental semiconductors that the Raman spectra of the amorphous form of the semiconductor is a broadened and shifted form of the polycrystalline form of the material. The Raman spectrum of the crystal can be useful as a guide to the identification of features and trends in the amorphous. Microcrystalline graphite samples show peaks at about 1580 and 1390 cm^{-1}, similar to the amorphous samples albeit much narrower. The origin of peak at 1580 cm^{-1} is associated with the mode in graphite (thus the name G-peak) while the feature at approximately 1390 cm^{-1} in microcrystalline graphite samples is associated with disorder in the samples. Thus the name D-peak for this feature. In graphite the magnitude of the D-line has been correlated with size of particles; following the procedure of Tuinstra *et al.*the intensity ratios I_D/I_G is often used to estimate the cluster size L_a.[2,6] This procedure is not justifiable for amorphous carbon. It is reasonable to conclude, however, that generally the larger the magnitude of the D peak the more the disorder in the film.

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This suggests that the relative differences in the ratio of the D peak to the G peak are due to differences in the structure of the carbon in samples, those with the largest D peak have the most disorder. What causes the large difference in ratio of the two peaks between the multilayer and other samples? While it may be supposed that the carbon is more disordered in the multilayer samples, the source of the disorder can not be ascertained with any certainty.

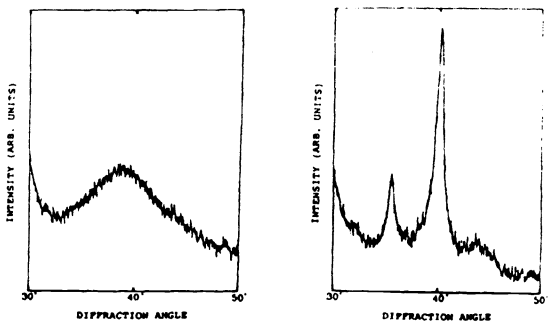


Fig. 7. X-ray diffraction results of W/C multilayer (left) and W/C layer pair sample (right). Peaks in the layer pair case indicate the crystal structure of the tungsten.

We have circumstantial evidence that this is an interfacial effect. In the multilayer films the deposited carbon grows on an amorphous tungsten layer, while in the other cases it is deposited on crystalline tungsten or silicon.

It has been reported that magnetron sputtered tungsten layers are amorphous when the film is thin (about 15Å) but by the time that the thickness increases to about 50Å the tungsten is polycrystalline.[7] In our case, the thickness of tungsten is about 20Å for each layer of multilayer samples and about 450Å for the W/C layer pair samples. We have examined the structure of tungsten in multilayer and single layer pair samples via x-ray diffraction. The tungsten in multilayer samples is amorphous whereas, in single layer pair samples is polycrystalline (see Fig.7). This, then, could account for the differences in the ratio of the I_D/I_G. The carbon in multilayer samples might have grown on a-W while in W/C layer pair samples might have grown on c-W.

6. CONCLUSION

Raman spectroscopy was used to characterize W/C multilayers. There are two main features, a peak at about 1560 cm^{-1} and shoulder at about 1370 cm^{-1}. Deconvoluted with Gaussians there yield two peaks one at 1420 cm^{-1} (the D-peak) and one at 1570 cm^{-1} (the G-peak). From the amorphous carbon Raman spectrum we estimated that the carbon in multilayered samples may be more disordered than the carbon in single layer pair samples. There is evidence that this is an interfacial effect related to the structure of the layer that the deposited carbon film grows on.

7. ACKNOWLEDGEMENTS

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