

THE EFFECT OF OXYGEN ON THE STRUCTURE OF ANNEALED W/C MULTILAYER THIN FILMS

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(Received 24 January 1991 by A. A. Maradudin)

W/C multilayers were prepared on unheated Si substrates by RF sputtering method. Raman scattering, x-ray diffraction and Auger depth profile were used to characterize the structure of the as-prepared and annealed multilayers in the range of 300 to 800 C. The results were compared in samples subjected to three different annealing conditions: 1) in air, 2) in high purity Ar atmosphere and 3) in evacuated and sealed ($\sim 10^{-4}$ torr) ampules. The result of Auger profiles indicates that the penetration depth of oxygen in the films depends on the annealing conditions, annealing temperature and layering structure. It also shows the loss of compositional modulation and the oxidation of W in the region reached by the oxygen. Raman scattering from the oxidized top layer(s) displays a spectrum with lines associated with crystalline tungsten oxide and segregated microcrystalline graphite particles

Artificial multilayer structures composed by alternating ultrathin layers of light elements (C, Si,...) and heavy elements (W, Mo,...) are of interest for applications as x-ray optical mirrors [1-3]. Due to the absorption of x-ray radiation, the temperature of the device can be significantly high, therefore for some applications good thermal stability is required. Several recent publications [4,5] described the effects of annealing on the structure of W/C multilayers. However, to our knowledge no systematic study has been reported showing the effects of oxygen during the annealing process.

In this study, W/C multilayers were subjected to thermal annealing in the presence of oxygen. The induced structural changes were characterized using Raman scattering (RS), Auger electron spectroscopy (AES) and x-ray diffraction (XRD). The results indicate the presence of oxygen to a depth which depends on the annealing condition and the layering structure. It is also found that the oxidized layer consists of a mixture of crystalline WO_3 and large crystalline graphite particles.

W/C multilayers with a nominal d spacing varying from 2.5 to 14 nm were prepared on unheated Si substrates by RF sputtering method. From the position of the low angle XRD peaks, d spacings within 5% of the nominal values were obtained. All samples consisted of 30 layer pairs and the W layer (top layer) thickness was kept at 2 nm. The W/C were annealed in the range of 300 to 800 C under the following three conditions: 1) in air, 2) in ultra-high purity Ar atmosphere and 3) in evacuated ($\sim 10^{-4}$ torr) and sealed quartz ampules.

Figure 1 shows the first order Raman spectra from the as-prepared multilayers, the nominal C layer thickness is indicated at the right side of each curve. The Raman intensity in the vertical axis was recorded using the same scale. All Raman spectra consisted of a main feature centered at about 1500 cm^{-1} and weaker signals at lower frequencies. It is observed that for all frequencies, the Raman intensity increases monotonically with the increase in

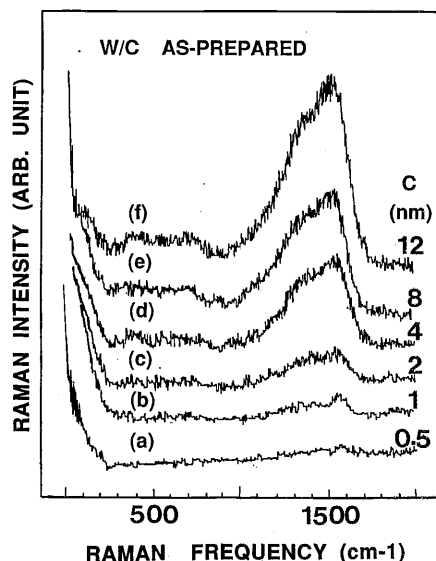


Figure 1. Raman Spectra of as-prepared W/C films. The W layer thickness was 2 nm. The C layer thickness was (a) 0.5, (b) 1, (c) 2, (d) 4, (e) 8, & (f) 12 nm.

the carbon layer thickness. Spectra similar to these have been previously related to amorphous carbon structures in which carbon atoms are mainly in the threefold coordination [6]. Details in the shape of the main feature may be associated with variations in atomic coordination and local structural ordering [6,7]. For all

as-prepared samples high angle XRD data indicates that the W layers are also in the amorphous state.

In fig. 2 the Raman spectra of two W/C (2/12 and 2/0.5) films are compared after annealing at 400 C for 1 hr under the three different annealing conditions mentioned above. Two obvious changes are observed in the spectra, namely: i) the appearance of sharp Raman lines at about 250, 700 and 800 cm^{-1} (marked with arrows) and ii) the splitting of the main Raman feature into two broad peaks located at 1350 and 1550 cm^{-1} . Notice that the three sharp lines were almost undetectable in both samples annealed in Ar atmosphere. From reference Raman spectra in standard samples [8] and also from the Raman and XRD measurements on thin films of WO_3 and WO_x/C multilayers, these three sharp Raman peaks are associated with the formation of

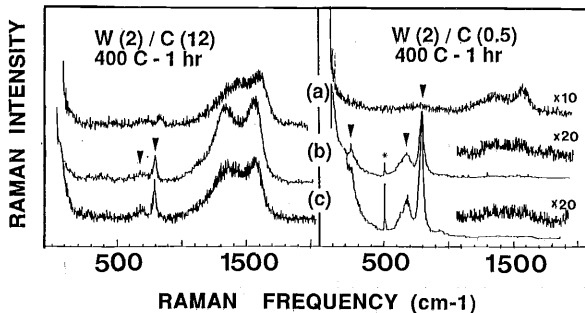


Figure 2. Raman spectra of two W/C thin films (2/12 and 2/0.5) after 400 C annealing for 1 hr under (a) in Ar atmosphere, (b) in evacuated and sealed ampule, and (c) in air.

crystalline WO_3 structure (triclinic and orthorhombic). The fact that the broad amorphous carbon line became a well defined doublet for the 2/12 sample as well as the appearance of a weaker but similar signal on the 2/0.5 sample after annealing in air and in an ampule suggests that somehow oxygen has catalyzed the observed structural changes. According to many other authors, the changes are indicative of a transformation from amorphous carbon to microcrystalline graphite [9]. What is remarkable is that these changes occurred at annealing temperatures as low as 400 C. If oxygen is avoided during the annealing, much higher temperatures (>1000 C) are needed to observe comparable changes in the Raman spectrum [10]. The increase in the Raman intensity after annealing at 400 C is probably related to a larger Raman cross section for the microcrystalline graphite. The narrow line at about 520 cm^{-1} (labeled with *) for the 2/0.5 samples is the first order Raman peak from the crystalline Si substrate. This implies that for the photon energy of the excitation the sample is more transparent due to the formation of a thicker WO_3 layer and also to the loss of carbon, most likely in a CO vapor form.

Figure 3 illustrates the Auger depth profiles recorded from a sample with W(2)/C(8) before (a), and after annealing in air for 1 hr at 400 C (b), 500 C (c) and 600 C (d). Figure 3(a) is the Auger profile recorded from the top four layer pairs of an as-prepared sample. Compositional modulation of the W signal is clearly shown, the modulation of the C signal is not as well resolved. The as-prepared sample only contains a very thin surface W oxide due to the air exposure. Annealing in air at 400 C for 1 hr caused the oxidation of the first W-C layer pair, as shown in fig. 3(b), without disturbing the original layer structure of the remaining layers as determined from the low angle XRD analysis [11]. The Auger profile obtained after annealing at 500 C reveals two distinct compositional regions as displayed in fig. 3(c). The top 2/3 portion of the film basically consisted of a mixture of WO_x and a small amount of C. The remaining 1/3 portion of the

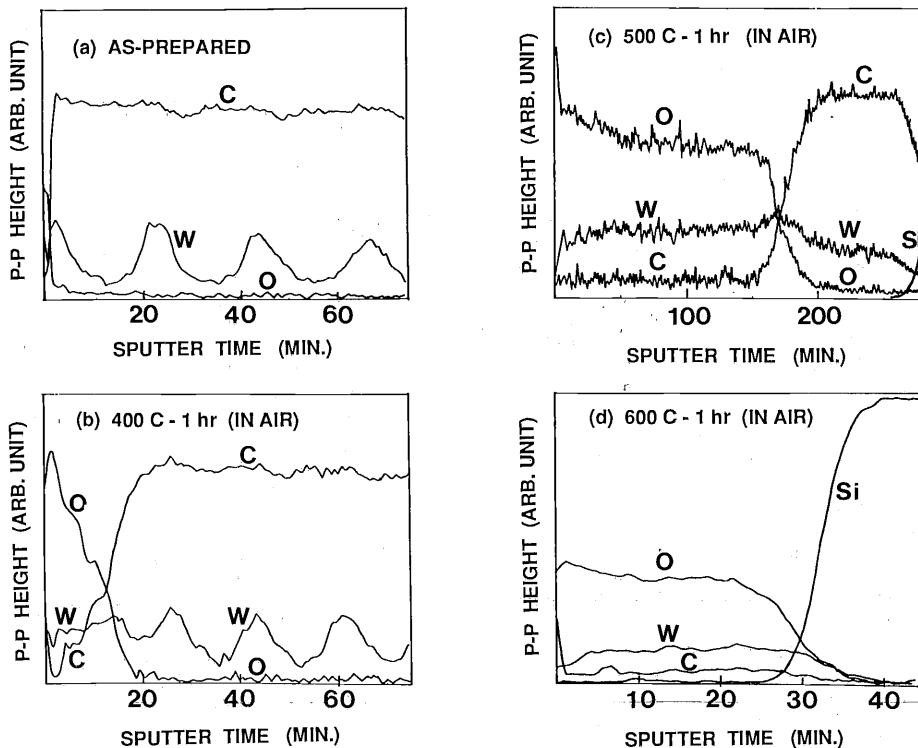


Figure 3. Auger depth profile recorded from the W(2)/C(8) sample: (a) as-prepared, and after (b) 400 C, (c) 500 C, and (d) 600 C annealed in air for 1 hr. The sputter was 0.7 nm/min. (wrt Ta_2O_5) in (a)-(c) and 3.5 nm/min. in (d).

film was oxygen free and still kept its original layer structure as measured by XRD and RS. The modulation of the W signal is not resolved in the bottom region of the Auger profile probably due to the ion beam mixing effect in the long profile process. The 600 C annealed film, similar to the top portion of the profile in 3(c), mainly contained WO_x mixed with a very small amount of C. The original layer structure was totally destroyed and the majority of the C material has been removed upon annealing at 600 C.

The corresponding Raman spectra of figs. 3(a-d) are displayed in figs. 4(a-d). It is observed that with increase in the annealing temperature the intensity of the WO_3 lines (marked with arrows) increased and the two microcrystalline carbon lines became narrower but their intensities decreased. The lines at 520 and 950 cm^{-1} (marked with *) in (c) and (d) are associated with the first and second order Raman lines of the crystalline Si substrate. According to the Auger profiles, annealing at 400 C only oxidized the first W-C layer pair. After using low energy (1.5 keV) Ar ion beam to remove this oxidized top layer the recorded Raman spectrum was very similar to that observed in the as-prepared sample. Thus, the carbon Raman signal in curve (b) is the superposition of two components: one obtained from the microcrystalline graphite particles formed in the first layer pair and the other from the undisturbed amorphous layers from beneath. Since the oxygen reacted with most of the layer pairs (about 2/3) in the 500 C annealed sample, we believe that the carbon signal comes mainly from the microcrystalline graphite particles in the oxidized region. The latter is also the case for the sample annealed at 600 C, fig. 3 (d), however, the Raman intensity of the graphite lines is significantly weaker because most of the carbon has effused out probably in the form of CO gas.

In summary, amorphous W/C multilayers have been annealed under various annealing conditions. If oxygen is present, both W and C layers oxidized to a depth which increases with the increasing annealing temperature and the amount of oxygen during the annealing, but decreases with the increasing thickness of the C layers. In the region reached by oxygen, the compositional modulation is lost and crystalline WO_3 and graphite particles are formed. Although part of the carbon effuses out of the multilayer during the annealing, it is observed that oxygen catalyzes the nucleation and growth of graphite particles at very low temperatures.

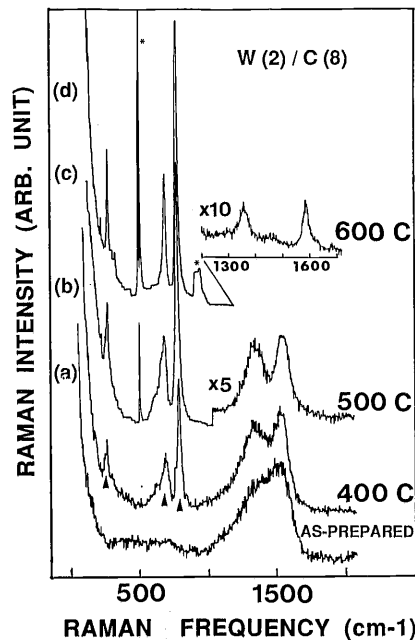


Figure 4. The corresponding Raman spectra of the W(2)/C(8) sample under conditions as indicated in Fig.3 (a-d).

Acknowledgement.

We would like to thank the encouragement of S.R. Ovshinsky of ECD. One of us, J.G.H. acknowledges the Consejo Nacional de Ciencia y Tecnologia for the partial support (contract # 891541).

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