Optical Emission Spectroscopy Study Of RF Sputtered A-C/WOX Interface

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Abstract: Amorphous carbons on tungsten oxide (a-C/WO_X) bi-layers were deposited on silicon substrates by rf sputtering. The WO_X layers were obtained from a pure tungsten target, in a gas mixture of argon and oxygen, whereas those of a-C were obtained from a graphite target, in pure argon plasma. The reactivity of the a-C/WO_X interface and the ion bombardment effects have been studied by Optical Emission Spectroscopy (OES) technique. The OES spectra show that the a-C/WO_X interface is reactive in accordance with previous results obtained by X-ray reflectometry. The inter-diffusion depth is estimated to be greater than 56 nm. Emission lines of W are still observed even after an ion bombardment time of about 45 minutes. This result confirms the presence of the Knock-on effect.

Keywords: Carbon, tungsten oxide, interface, ion bombardment, optical spectroscopy, RF sputtering

I. Introduction

Transition metal carbides, carbonitrides and oxycarbides have generated great interest both in academic study and industrial applications. They are expected to be widely used as hard coating materials [1-5]. Thin films of ternary materials can be deposited by different techniques, such as Chemical Vapour Deposition (CVD), reactive sputtering and glow discharge [6-8]. Another technique that can be used to produce these films is the deposition of a multilayer structure [9]. In a previous study [10], we have shown that it is possible to use this technique to obtain oxycarbide (WOxCy) thin films from a-C /WO_X multilayers. In the present work, we present some results of further study of similar structures in a-C/WO_X bi-layers using the surface analysis by Optical Emission Spectroscopy (OES) technique.

II. Experimental details

Amorphous carbons on tungsten oxide (a-C/WO_X) bi-layers were deposited, on crystalline silicon substrates, by radiofrequency (RF) sputtering. WO_X films were obtained from a pure tungsten target in a gas mixture of argon and oxygen, whereas those of a-C have been deposited from a high purity graphite target in pure argon. The argon pressure and RF power were respectively maintained to 10^{-2}Torr and 250Watts during the deposition. Before introducing the sputtering gas into the deposition chamber, a low pressure of about 10^{-6}Torr is achieved using an Alcatel oil diffusion pump. The thickness of the WO_X and a-C layers is about 100nm.

The experimental technique OES, we used in this study, consists of an optical spectrometer which allows measurements of the intensity of the optical signal as a function of the wavelength of light emission occurred during the bombardment of the surface sample by a beam of krypton ions. The details of this apparatus, which has served in several previous studies, are given in references [11-13]. We recall here that Kr^+ ions are formed by electrons impact on a high purity (5N) krypton gas and are extracted with energy of 5 keV. The ion beam is focused onto the surface of the sample with a current density of several μA/mm^2. The target constituents, ejected in excited electronic states can de-excite by emitting light radiations whose wavelengths are measured in the spectral range from near UV to the visible with a resolution approaching the Angstrom. The sample is introduced in a vacuum chamber and the residual pressure achieved is better than 10^{-7} Torr. For convenience, optical emissions produced during the ion bombardment of the sample surface are detected in a direction perpendicular to the ion beam direction. The optical emissions are analyzed by a Jobin Yvon HR-320 monochromator, with a focal length of 320 mm, equipped with a holographic grating of 1800 grooves/mm. The selected light signal is received by a Hamamatsu R4220P photomultiplier type, which is sensitive to wavelengths lying between 1900 and 6500A. The whole detection chain is controlled by a microcomputer, which allows also the acquisition of data using the PRISM program. The analysis technique is known under various acronyms [14], we develop it under acronym OES (Optical Emission Spectroscopy). The average sputter etching speed, in conditions mentioned above, is of the order of 24 nm/min.

III. Results and discussion

Figures 1 and 2 show the typical OES spectra of a-C/WO_X bi-layers in the wavelengths range where appear respectively the emission lines of silicon and tungsten. To study the profile of the analyzed bi-layers, we have made short scans in the wavelengths range between 249 nm and 254 nm for Si (area A in Figure 1) and between 426 and 431 nm for W (area B in Figure 2) after different bombardment times. The as obtained spectra for Si and W emission lines are reported in Figures 3 and 4 respectively. These spectra show that after the first few minutes of ion bombardment, the lines of W are already at their maximum. This result suggests that the a-C/WOx interface is reactive. Such behavior is in perfect agreement with that obtained in a previous study by X-ray reflectometry [10]. Also, we note the appearance of Si lines after the first eight minutes of bombardment. Taking into account the average etching speed in our conditions, which is about 24 nm/min, the Si lines appear after etching around 190 nm. This value is very close to the total thickness (200 nm) of the a-C/WOx bi-layer.

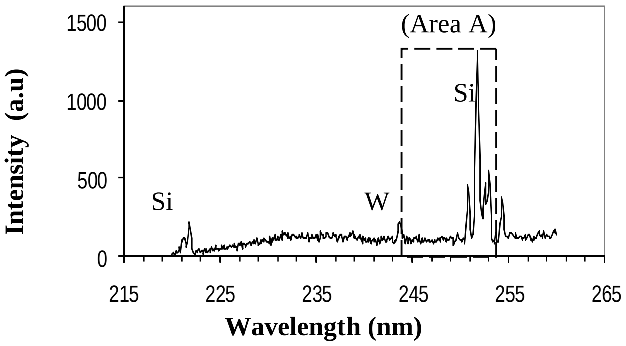

Figure 1: OES Spectrum in the spectral region where appear the Si lines

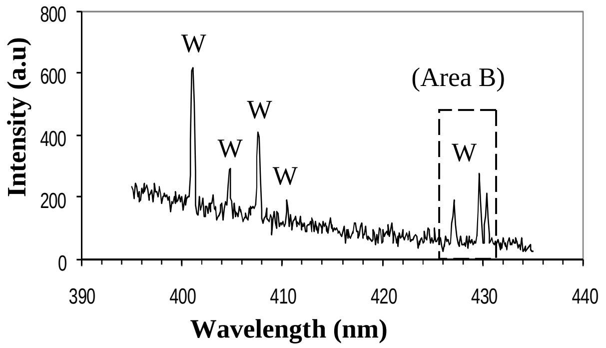

Figure 2: OES Spectrum in the spectral region where appear the W lines.

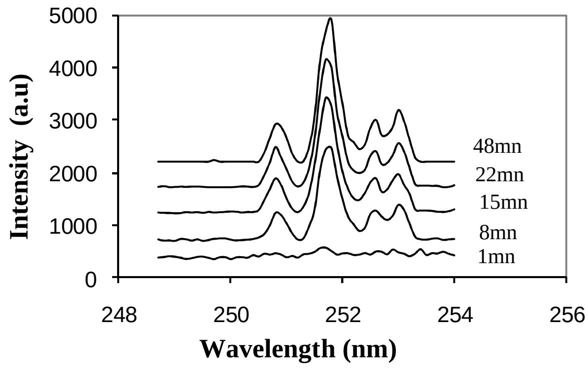

Figure 3 : Evolution of Si lines (area A in fig.1) OES spectra versus sputter etching time

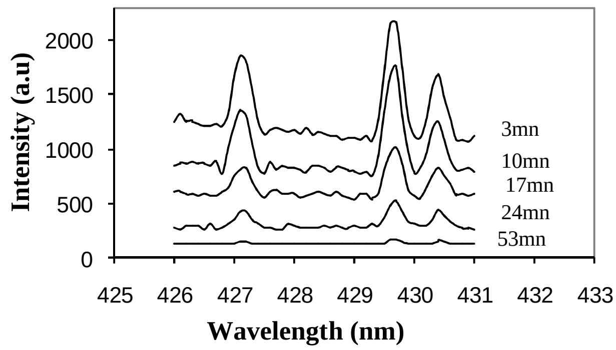

Figure 4 : Evolution of W lines (area B in fig.2) OES spectra versus sputter etching time

Moreover, we note, in Figure 4, that the W lines continue to appear even after a sputter etching time of 24 minutes. This etching time corresponds to an etched thickness of about 576 nm. This value is much greater than the total thickness (almost three times greater) of the a-C/WOx bi-layer. This result shows clearly the existence of the knock on effect : the W atoms are injected deeply into the Si substrate during the ion bombardment.

Figure 5 shows the depth profile, of the a-C/WOx bi-layer, obtained from the 251.6 nm and 429.5 nm lines (Si and W lines). The inter-diffusion layer thickness could not be calculated from this figure because we were not able to follow the C emission lines, which are situated outside the range of wavelengths explored by the photomultiplier. However, one can estimate this thickness from the W line profile. Indeed, the intensity of this line reaches its maximum after the first few minutes (less than 3 mn) of sputter etching. Such a sputter etching time removes about 72 nm of the top layer. Then, the W atoms are diffused to more than 28 nm in the a-C layer. Assuming that the inter-diffusion of C and W (at the interface) is symmetric, we can estimate the WCxOy layer thickness to be greater than 56 nm.

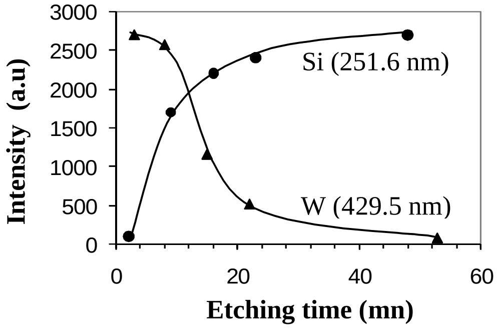

Figure 5: Depth profiles of the 251.6 nm (Si) and 429.5 nm (W) lines versus sputter etching time

IV. Conclusion

In this work, we studied a-C/WO_X bi-layers deposited by RF sputtering at 250W on crystalline silicon substrates. The study is accomplished using the technique of surface analysis by Optical Emission Spectroscopy (OES). We have shown that the a-C/WO_X interface is highly reactive (a result in perfect agreement with a previous study by X-ray reflectometry). The inter-diffusion depth is estimated to be greater than 56 nm. Furthermore, we showed the existence of the knock-on effect, which is clearly observed for the W atoms injected in depth into the c-Si substrate during ion bombardment of the surface sample.

V. References

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