Surface Morphology of Au and Ag Nanocluster-Containing Amorphous Hydrogenated Carbon Studied by XPS of Adsorbed Thiophene

Ivan R. Videnović

Abstract. Amorphous hydrogenated carbon containing gold and silver nanocluster inclusions (a-C:H/Au and a-C:H/Ag, respectively) has been produced in combined magnetron sputtering of a metallic target and plasma-assisted CVD in argon/methane atmosphere under vacuum conditions. Surfaces of the samples deposited on the grounded and –150 V dc biased substrates are studied by XPS of adsorbed thiophene (C\textsubscript{4}H\textsubscript{4}S). Higher amount of sulfur bound to the metallic atoms, revealing higher metal exposure at the surface, is found on the biased a-C:H/Au samples than on the grounded ones. In a-C:H/Ag, metal exposure at the surface is enhanced both by biasing and by Ag cluster coalescence into bigger agglomerates.

INTRODUCTION

Various applications of amorphous hydrogenated carbon (a-C:H) thin films show that metallic or carbidic nanosized inclusions improve coating properties such as wear resistance [1-4], biocompatibility [5,6], or solar selectivity and aging properties [7-9]. In structural studies of reactively sputtered titanium-containing a-C:H (a-C:H/Ti) Schüler et al. [10] noticed that surface analysis by x-ray photoelectron spectroscopy (XPS) yields systematically lower Ti content than the bulk analysis by Rutherford backscattering (RBS). Using the same deposition method and gold nanocluster-containing a-C:H as a model system, Videnović et al. [11] showed that this discrepancy originates from the topmost metallic clusters coverage with a very thin layer of a-C:H, which occurs whenever the deposition is made onto substrates kept on wall (ground) potential. Partial baldness of the topmost clusters is encountered when substrates are additionally biased with negative dc voltage [11].

In this work we provide supplemental experimental evidence of the previous conclusions [11] from the XPS study of the adsorbed sulfur-containing organic compound thiophene (C\textsubscript{4}H\textsubпи S) at the surfaces of a-C:H/Au and a-C:H/Ag. These coatings are obtained in combined magnetron sputtering of metallic target by argon, and plasma-assisted chemical vapor deposition (CVD) of methane. Counting on the known tendency of sulfur to bind to noble atoms, our expectations in this experiment were that surface metallic nanoclusters baldness or their coverage with a layer of a-C:H should affect binding of sulfur to Au and Ag.
EXPERIMENT

The deposition chamber is pumped down to the base pressure below $10^{-6}$ mbar. Argon and methane are fed into the chamber in a mass flow ratio $\text{Ar} / \text{CH}_4$ of 1.5. Using a throttling valve, the total gas pressure during deposition is kept at about $6 \times 10^{-3}$ mbar. To run the plasma, a water-cooled magnetron, capped by Au or Ag target is driven by bipolar-pulsed dc power at 50 kHz. The substrate holder is kept either grounded or biased at $-150$ V dc. Since that is the parameter that determines metallic exposure at the sample surface [11], we shall use the terms grounded and biased to denote samples deposited without and with substrate bias voltage, respectively. The distance between the substrate (1×1 cm$^2$ Si wafer, 0.5 mm thick, 40–70 $\Omega$cm resistivity) and magnetron target was about 10 cm. The thickness of the deposited coatings was about 20 nm, as controlled by quartz crystal monitor. To determine relative metallic content at the surface, without sample exposure to the air, their transfer from the deposition to the XPS ultra-high vacuum (UHV) chamber is made via an intermediate and independently evacuated chamber. For the reference metallic core level measurements, Au and Ag monocrystalline samples are used. After first reference and “as deposited” XPS measurements, samples are taken out from the UHV, and several drops of liquid thiophene (purity >98%) are put on the surface so that entire sample area is covered. Once C$_4$H$_4$S has entirely evaporated, samples are put again into UHV and subjected to XPS analysis. In general, low amount of sulfur is detected at the surface, at maximum about 5 at.%. As a consequence, noisy XPS signals of the S 2$\text{p}$ region are obtained, in spite of high measurement statistics. More experimental details can be found in Ref. 12.

RESULTS AND DISCUSSION

Figure 1a shows the S 2$\text{p}$ core levels of sulfur detected on a monocrystalline gold reference sample. After subtraction of the Shirley background [13], the fitting of the experimental data by convolved Gauss and Lorentz profiles is made using three S 2$\text{p}_{3/2}$–S 2$\text{p}_{1/2}$ doublets with fixed energy separation of 1.18 eV and intensity ratio between $j = 3/2$ and $j = 1/2$ components of 1.71 [14]. The best fit values of binding energies of the S 2$\text{p}_{3/2}$ core level are attributed to S–Au bonds (161.9 eV, [15]), sulfur in C$_4$H$_4$S (163.8 eV, [14]), and S–O bonds (167.8 eV, [16]). Figure 1b shows results of the same 3-doublet fitting procedure applied to a-C:H/Au grounded samples of 4.6 at.% and 19.4 at.% Au and biased samples of 6.3 at.% and 16.8 at.% Au. The C$_4$H$_4$S-originated S 2$\text{p}_{3/2}$ is a dominant peak in all spectra. The relative content of sulfur measured on each sample is given in the figure. Although very small, sulfur content is regularly higher in the biased than in the grounded samples. Besides, the shapes of biased samples spectra show a shoulder at about 162 eV that originates from S–Au bonds, and is related to the higher gold exposure at the sample surface.

The same 3-doublet fitting procedure is applied to the silver monocrystalline reference sample, two grounded a-C:H/Ag samples of 12.0 at.% and 19.9 at.% Ag, and two biased samples of 5.0 at.% and 8.6 at.% Ag. The results of fitting the S 2$\text{p}$ spectrum after thiophene evaporation from the Ag reference sample are shown in Fig. 2a. Again,
the S $2p_{3/2}$ position at 161.8 eV is assigned to the S–Ag bonds and the S $2p_{3/2}$ at 164.1 eV to the sulfur in C$_4$H$_4$S. The contribution of the S–O bonds at 167.8 eV was negligible in the case of Ag reference sample. All a-C:H/Ag samples show strong peak related to sulfur in C$_4$H$_4$S, but also, in all spectra the shoulder at about 162 eV related to S–Ag bonds is obvious. Here, the grounded samples adsorbed higher amount of sulfur, what may be explained by pronounced coalescence of surface Ag clusters in both grounded and biased cases [12]. Also, in the grounded samples the C$_4$H$_4$S-related sulfur peak is stronger. Higher relative contribution of the S–Ag bonds-related peak at 162 eV in the biased 8.6 at.% Ag sample indicates higher surface exposure of silver.

In conclusion, XPS analysis of thiophene adsorption at the surface of Au and Ag nanocluster-containing a-C:H indicates higher surface metallic exposure in the samples deposited with substrate bias voltage in comparison to the grounded ones. In a-C:H/Ag, this effect is partially hidden by enhanced silver surface agglomeration.

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FIGURE 2. a. Sulfur S 2p spectrum at the Ag reference sample, fitted with two S 2p\(^{1/2}\) – S 2p\(^{3/2}\) doublets. b. Normalized S 2p spectra on a-C:H/Ag grounded and biased samples, together with the Ag reference. A shoulder at about 162 eV, related to the S–Ag bonds, is observed in all a-C:H/Ag spectra.

REFERENCES