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Study of the Au-Cr bilayer system using x-ray reflectivity, GDOES and ToF-SIMS

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Abstract

We study a Au (25 nm)/Cr (10 nm) bilayer system as a model of mirror for the soft x-ray energy range. The Au and Cr thin films are a few nanometers thick and are deposited on a float glass substrate. The sample is characterized using three complementary techniques: soft x-ray reflectivity (XRR), glow discharge optical emission spectrometry (GDOES) and time of flight secondary ion mass spectroscopy (ToF-SIMS). XRR provides information about the thickness and roughness of the different layers while GDOES is used to obtain the elemental depth profile of the stack and ToF-SIMS to obtain the elemental and chemical depth profile. GDOES and ToF-SIMS have both a nanometer depth resolution. A coherent description of the bilayer stack is obtained through the combination of these techniques. It consists in five layers namely a surface contamination layer, a principal gold layer, a Au-Cr mixed layer, a Cr layer and another contamination layer at the top of the substrate.

Keywords: x-ray mirror; gold; chromium; x-ray reflectivity; ToF-SIMS; GDOES

Introduction

Gold thin films are used in grazing incidence x-ray reflectivity mirrors in the 100-1500 eV soft x-ray region on synchrotron beamlines because of its flat reflectivity performance [1]. In order to provide a good adhesion with silicon or fused silica substrates, a binding layer of chromium is often used. These mirrors should exhibit no interdiffusion in order to get high and stable performances and thus need to be carefully characterized. To this purpose we use a combination of non-destructive techniques: soft x-ray reflectivity (XRR), glow discharge optical emission spectroscopy (GDOES) and time of flight secondary ion mass spectrometry (ToF-SIMS). The main goal is to determine the thickness of the different layers and interlayers and get some knowledge about the interactions between the layers or at the top of the substrate or at the top of the stack. This kind of methodology has been already used successfully for the study of nanometer periodic multilayers designed for x-ray optics, see Refs. [2–6] for example.

Experimental details

The Au/Cr bilayer sample was prepared by electron beam evaporation from high purity Au and Cr targets. Its designed structure was : Au / Cr / SiO_2 substrate. 25 nm Au and 10 nm Cr layer thicknesses were targeted, respectively. The substrate was a float glass. After its preparation the sample was stored in ambient conditions.

XRR measurements [7] were performed at the reflectivity beamline BL3 [8] of Indus-2 synchrotron radiation source. A monochromatic 1500 eV incident photons irradiated the sample and $\theta - 2\theta$ scans were recorded from 0 to 16°. The intensity reflected by the sample, as measured by a silicon photodiode detector (International Radiation Detector Inc.) having a 100 % internal quantum efficiency, was normalized to the one obtained without sample to obtain the reflectance value. A nickel mesh of 90% transmission was mounted prior to the sample to measure the time variation of the incident photon flux. This enables one to account the effect of photon flux variation due to the fall in electron beam current in the storage ring. The fit of the XRR curve enable getting structural information about the studied stacks: thickness, density and roughness of the various layers.

The GDOES experiment [9] was performed with an apparatus Profiler 2 from Horiba Scientific. A 30 W pulsed RF power generated a plasma in Ar gas which pressure was 500 Pa. The pulse frequency and duty cycle were 3000 Hz and 0.25 repsectively. The plasma is used to both sputter the sample and excite the elements, making them emit characteristic lines. The width of the glow discharge spot on the sample was 4 mm. It took less than 2 s to sputter the whole stack. However, the fast acquisition of the optical signal makes it possible to analyse ultra-thin layers.

For the TOF-SIMS analysis [10], performed with an TOF.SIMS V apparatus from ION-TOF GmbH, a 1 keV, 50 nA Cs^+ ion beam was used to sputter a crater which size was 300 x 300 µm. The analysis was made on a 100 x 100 µm area at the centre of the crater by using 25 keV, 1 pA Bi^+ ions. First, a mass sum-spectrum was obtained by looking at the time of arrival of the ion on the detector, in order to get all the relevant ions. Then, the intensity of each selected ion (of a given mass) was followed as a function of the sputtering time. This time scale is not simply correlated to the thickness. Let us also note that the difference between the yields of two elements is not related to the difference of concentrations of these two elements (SIMS is not a quantitative technique, mainly due to the matrix effects). The analysis is made by detecting the following positive ions : Si^+, CsO^+, $CsSiO^+$, $CsCr^+$, $CsCrO^+$, $CsAu^+$, $CsAuCr^+$, Cs_2C^+, $CsNa^+$ and $CsCa^+$. The three first ones are chosen to probe the substrate; $CsCrO^+$ can indicate the possible

formation of a Cr oxide; $CsAuCr^+$ can indicate the possible formation of a AuCr alloy or solid solution; the three last ones are related to contamination and impurities. Except Si, all ions are the combinations of Cs with the element of interest. Cs_2C^+ is chosen instead of CsC^+ owing to its higher yield.

Results and discussion

Figure 1 shows the measured and fitted soft x-ray reflectivity curves of the sample together. The best fit reveals that the bilayer is made of: C (2.0nm) / Au (23.8nm) / Cr (10.2nm) / SiO_2 substrate. The roughness at the three interfaces, C-on-Au, Au-on-Cr and Cr-on-SiO_2 are respectively 0.6, 0.8 and 0.7 nm. The optical indices of bulk Cr and SiO_2 were used, but for the Au film it was necessary to decrease the refractive index, real and imaginary parts, by 3% with respect to its bulk value. This suggests that the density of the Au film is slightly lower (≈4%) than the bulk value.

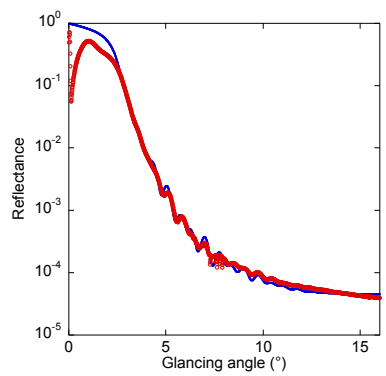

Figure 1: Measured (red dots) and fitted (blue line) soft x-ray reflectivity curves of the Au/Cr bilayer sample for 1500 eV incident photon beam.

We show in Figure 2 the GDOES profiles of the Au, Cr major elements as well as of Na, Ca, C, O impurities or contaminants elements. Sodium and calcium are the main impurities of the float glass substrate. Carbon can come from the contamination of the substrate prior the deposition and of the sample after its preparation. Oxygen is present in the glass substrate and in air. Three main zones with two transient zones can be identified:

- 0 – 0.11 s: the contaminated surface with the presence of all the studied elements except Cr. While the presence of carbon and oxygen is easily ascribed to the air contamination, this explanation does not hold for sodium and calcium. We suggest these atoms are surfactants and stay above the growing films during the deposition process.
- 0.11 – 0.53 s: the Au layer with a rather constant yield, while the yield of the other elements quickly decreases, except the Cr one increasing quickly at the end of this zone; the C signal, whose maximum is around 0.08 s, is quickly decreasing in this layer, suggesting no interphase between the contaminated and Au layers.
- 0.53 – 0.64 s: the Au-Cr transient zone marked by an oscillation of the Cr yield and a O peak. This could indicate a possible oxidation of the top of the Cr layer; at the end of the zone the decrease of the Cr yield is in phase with a slight shoulder of the Au yield.
- 0.64 – 1.08 s: the Cr layer with a yield slightly fluctuating.

- 1.08 – 1.22 s: the Cr-SiO_2 transient zone, where the Cr signal is decreasing while those of O, Na and Ca start to increase. A small peak of the C signal is also observed in this zone. We ascribe it to the superficial contamination of the substrate prior deposition.
- After 1.22 s: the substrate is reached.

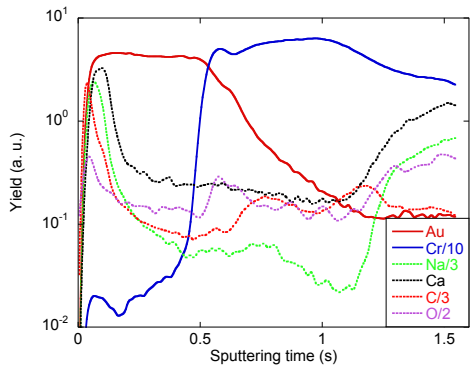

Figure 2: GDOES profiles of the sample. Major elements as well as impurities and contaminants are followed. The signals of Na and C are divided by a factor 3, the one of Cr by 10 and the one of O by 2.

We show in Figure 3(a) the Si^+, $CsSiO^+$, CsO^+, $CsCr^+$, $CsAu^+$, $CsAuCr^+$, $CsNa^+$ and $CsCa^+$ ToF-SIMS depth profiles and in Figure 3(b) the Cs_2C^+, $CrOCs^+$, $AuCrCs^+$ and $CsCr^+$ profiles. As in GDOES, five zones are identified:

- 0 – 15 s: contaminated surface; in this zone the sputtering regime is not yet well established; the superficial zone is probed; the profile of the carbon ion is shown after and confirms the existence of the contamination layer determined from the XRR analysis.
- 15 – 120 s: Au layer; the Au^+ yield is constant while those of the other ions are very weak; a low intensity Cr signal is significantly present as its intensity is higher than that in the silica substrate which can be considered as the background intensity; this SIMS Cr signal seems related to the low intensity tail of the GDOES Cr signal in the 0.11 – 0.53 s range (see Figure 2) and thus could show a small diffusion of Cr atoms toward the Au layer.
- 120 – 155 s: Au-Cr transient zone; both signals of $CsAu^+$ and $CsCr^+$ are present; more interesting the signal of $CsAuCr^+$ is present only in this zone; there is also of peak in the CsO^+ signal as in GDOES and also in the $CsCrO^+$ signal.
- 155 – 210 s: Cr layer; the $CsCr^+$ yield is more or less constant while those of the other ions are very weak; given the affinity of chromium for oxygen, a superficial oxidation of the Cr layer can take place owing to the presence of a non-negligible $CsCrO^+$ signal, whereas the CsO^+ signal is minimum.
- 210 – 270 s: Cr-SiO_2 transient zone; signals from both the substrate and the Cr layer are present.
- 270 – 365 s: SiO_2 substrate; the presence of Si^+ and CsO^+ ions is regular; the $CsCr^+$ signal drops steeply.
- Charging effect, after 365 s: after this sputtering time, charging effects coming from the insulating nature of the glass substrate prevent from further analysis under the same conditions.

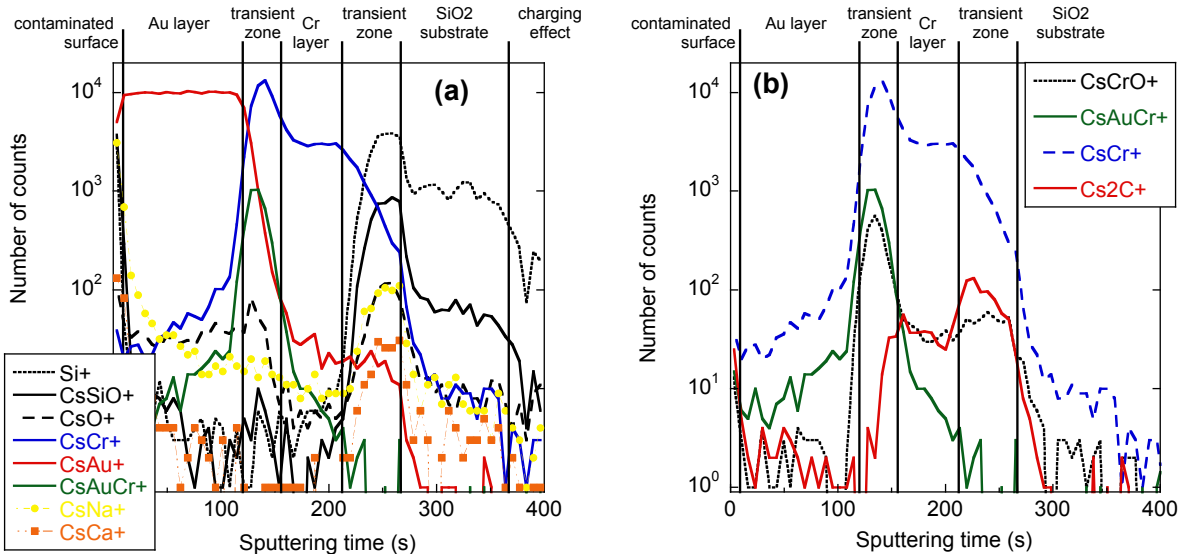

Figure 3: ToF-SIMS profiles of the sample. Major elements as well as impurities are followed.

The Cs_2C^+ SIMS signal is present in the contaminated layer where it decreases quickly when going deeper. This confirms the carbon presence as due to a surface contamination. The GDOES results confirm the presence of the carbon-contaminated zone. From the Cs_2C^+ profile it is also clear that some contamination takes place in the Cr layer and the transient zone between Cr and the substrate. In the Au and the mixed Au-Cr layers the intensity of the Cs_2C^+ signal is negligible. This is also confirmed by GDOES, where the signal of C is quite intense and shows some amount of carbon in the Cr layer, not in the mixed Au-Cr layer, and in the transient zone with the substrate. The Na and Ca impurities are mainly concentrated on top of the glass substrate and on top of the sample. The $CsCrO^+$ signal is only related to the Cr and mainly present at the two interfaces (Cr-Au and Cr-SiO_2).

There is a fair agreement between the structure of the Au/Cr/SiO_2 sample deduced from XRR, GDOES and ToF-SIMS measurements. The XRR analysis relies on a model of stack to determine the parameters of the different layers. In the fitting process, the roughness between the layers can be due to the geometry (height variation) or the chemistry (interdiffusion) or both of them. So, we ascribe the roughnesses at the Au-on-Cr and Cr-on-SiO_2 interfaces to the transient zones observed by GDOES and ToF-SIMS. The fitting results are not significantly improved even using a five-layer model, *i.e.* with Au-on-Cr and Cr-on-SiO_2 interlayers. In fact, the fitting results are rather good with a simple Au/Cr two-layer mode with a superficial contamination layer, Fig. 1.

Finally, we compare ToF-SIMS and GDOES profiles in Figure 4(a) for Au and in Figure 4(b) for Cr. To superimpose both curves, the GDOES sputtering time at 0.53 s is normalized with respect to the one of SIMS at 120 s and both yields are normalized to unity. The comparison is made on a linear scale. We can see that the SIMS profile presents a better dynamics, a more stable plateau and smaller tail. As expected, given the nano-thicknesses of the deposited layers, ToF-SIMS depth profiling seems better suited for this analysis. The dynamics of the signal is rather the same for GDOES and ToF-SIMS toward the low sputtering times whereas it is better for ToF-SIMS for long sputtering times. We could infer from this, that the ToF-SIMS sputtering process induces less mixing in the sample than the GDOES sputtering process or more probably that it is important to make the analysis without influence of the crater walls.

Indeed in ToF-SIMS the detected ions come from the centre of the crater (see the experimental details section) while in GDOES the detected signals come from the whole sputtered surface. It is interesting to note that both techniques give a Cr yield increase at the Au-on-Cr interface (around 130 s), however with much different amplitudes.

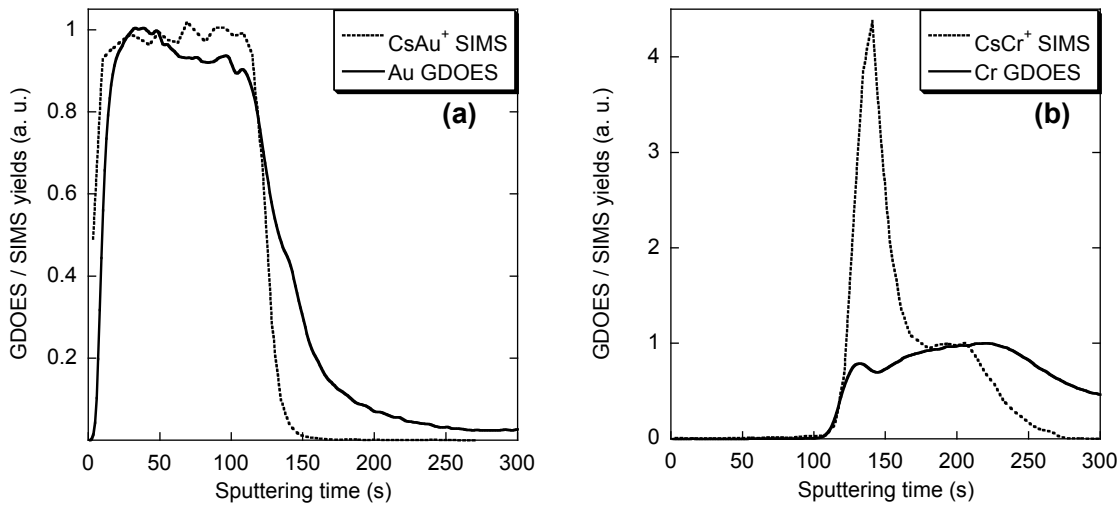

Figure 4: Comparison on a linear scale of the ToF-SIMS (dotted line) and GDOES (solid line) profiles of Au (a) and Cr (b) elements. The GDOES sputtering time is normalized to the ToF-SIMS one.

Conclusion

A coherent description of the Au/Cr/SiO_2 sample has been obtained by combining XRR, GDOES and ToF-SIMS measurements. XRR, which is non-destructive, enables getting the thickness of the different layers and interlayers as well determining that the gold film is slightly less dense than gold bulk. GDOES measurements are fast and enable obtaining elemental depth profiles of the major and minor elements of the sample. ToF-SIMS depth profiles present a larger dynamic range and bring supplementary chemical information in addition to the elemental one, particularly at the interfaces, as the association of an ion with another element can be detected. Finally, the structure of the sample, from the top to the bottom is:

- superficial layer, 2 nm thick, contaminated with oxygen and carbon; Na and Ca atoms are present as impurities coming from the substrate;
- gold layer, 24 nm thick, having slightly lower density that of bulk gold;
- Au-Cr transient layer, about 0.8 nm thick, where it is possible to find some AuCr mixing and oxidation of chromium on one or two layers (most probably Cr^{3+});
- chromium layer, 10 nm thick, contaminated with some carbon;
- Cr-SiO_2 substrate transient layer, about 0.7 nm thick; Na and Ca atoms are present as impurities on top of the substrate which is also contaminated by a small amount of carbon;
- float glass substrate.

Such a study shows the interest of combining complementary techniques in order to determine the in-depth composition of nanometer-thick multilayer stacks. The penetration depth of the radiation in gold being around 10 nm when used in total reflection mode, *i.e.* used as an x-ray mirror, our results

show that the choice of the thickness of the gold layer, 20 nm, was relevant. Indeed the presence of the interdiffusion layer at the Au-on-Cr interface would have deteriorated the optical performance of the stack if the gold layer would have been 10 nm-thick or thinner. This could be also the case if the mirror would be subject to a high thermal load, as it is generally the case for the first mirrors on synchrotron beamlines, which would broaden the interdiffusion zone.

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