EFDA–JET–CP(12)02/07

L. Marot, E. Meyer, M. Rubel, D. Ivanova, A. Widdowson, J.P. Coad,
J. Likonen, A. Hakola, S. Koivuranta, G. De Temmerman
and JET EFDA contributors

Performances of Rh and Mo Mirrors Under JET Exposure

Performances of Rh and Mo Mirrors Under JET Exposure

L. Marot[1], E. Meyer[1], M. Rubel[2], D. Ivanova[2], A. Widdowson[3], J.P. Coad[3], J. Likonen[4], A. Hakola[4], S. Koivuranta[4], G. De Temmerman[5] and JET EFDA contributors*

JET-EFDA, Culham Science Centre, OX14 3DB, Abingdon, UK

[1]Department of Physics, University of Basel, Association EURATOM-Confédération Suisse, Ecole Polytechnique Fédérale de Lausanne (EPFL), CRPP, CH-1015 Lausanne, Switzerland
[2]Alfvén Laboratory, Royal Institute of Technology, Association EURATOM-VR, 100 44 Stockholm, Sweden
[3]EURATOM-CCFE Fusion Association, Culham Science Centre, OX14 3DB, Abingdon, OXON, UK
[4]Association EURATOM-TEKES, PO Box 1000, 02044 VTT, Espoo, Finland
[5]FOM Institute DIFFER, Dutch Institute For Fundamental Energy Research, Association EURATOM-FOM, Trilateral Euregio Cluster, P.O. Box 1207, 3430 BE Nieuwegein, The Netherlands
** See annex of F. Romanelli et al, "Overview of JET Results", (23rd IAEA Fusion Energy Conference, Daejon, Republic of Korea (2010)).*

Preprint of Paper to be submitted for publication in Proceedings of the 20th International Conference on Plasma Surface Interactions , Eurogress, Aachen, Germany 21st May 2012 - 25th May 2012

ABSTRACT

The aim of this work was to provide a comprehensive surface characterization of rhodium and molybdenum mirrors exposed on the main chamber wall of JET during campaigns with carbon plasma-facing components. As determined using X-ray photoelectron spectroscopy, Secondary Ion Mass Spectrometry, Scanning Electron Microscopy and optical measurements the co-deposits formed on the mirrors were composed of C, Be, Ni, Mo and Fe. Most of the metallic elements on the surface were in the oxidized states. After removing a part of the film by sputtering with Ar^+ ions, Mo carbide state was studied by XPS. The reflectivity measurements showed the dependence of the thickness of the deposited film on the optical properties of the mirror: a thinner film on the Mo mirrors results in an identical reduction in reflectivity as that seen on the exposed Rh mirror.

1. INTRODUCTION

Due to the high level of neutron radiation expected in ITER, viewing the plasma directly will not be possible. Therefore, metallic mirrors are foreseen to play a key role in guiding the plasma light towards the optical diagnostics. As these so-called First Mirrors (FM) directly view the plasma, they will be subjected to a harsh environment of particle fluxes due to charge exchange neutrals and neutrons, as well as UV, x-ray and gamma radiation. Therefore, the performance of the mirrors will be crucial for the operation of all optical diagnostics [1, 2]. On the request of the ITER Design Team, the First Mirror Test (FMT) has been carried out at JET [3, 4]. Two experiments at JET with carbon walls, in 2005-2007 and in 2008-2009, have been realized [4, 5].

Molybdenum and rhodium are two important candidate materials for FMs. Mo, due to its low sputtering yield, is more advantageous under erosion conditions while Rh provides better reflectivity (over 90%) in the visible range [6]. Rh has also low chemical reactivity, preventing oxide and carbide formation. In the case of polycrystalline mirrors composed of many grains with random orientation of faces, the sputtering yield can vary strongly over the material surface depending on the crystallographic plane of each individual grain and its orientation with respect to the incoming particle flux [7]. It is also important to keep the surface relief pattern i.e. the roughness of a polycrystalline mirror small compared to the wavelength of reflected light in order to minimize the effect of diffuse reflection in the measurements. Generally, this indicates that the mirrors must have small grain sizes and preferably similar crystal orientation to be homogeneously sputtered. These requirements can be fulfilled, for instance, by using a single crystal or by coating the surface with nanometer-size crystallites. Due to technological difficulties in producing large size Mo single crystals, coating might be considered as an alternative [8]. The preparation of such coated mirrors was reported in our previous papers [6, 9] in laboratory scale and large scale mock-ups ($\phi = 110$ mm) [10].

As a consequence of Plasma-Wall Interactions (PWI), the mirror surface properties will be modified in a reactor-class device. The ongoing studies aim at (i) the mitigation of the detrimental effects of PWI and (ii) development of cleaning methods [11]. Therefore, it is absolutely crucial to fully understand the morphology of mirror surfaces after exposure to tokamak plasmas. This work

provides an overview of a comprehensive surface characterisation of the Rh coated Mo substrate [6] and the polycrystalline Mo mirrors exposed in the main wall of JET in 2008-2009.

2. EXPERIMENTAL

The study was carried out by means of X-ray Photoelectron Spectroscopy (XPS), Secondary Ion Mass Spectrometry (SIMS), Scanning Electron Microscopy (SEM) and optical methods. Total and diffuse reflectivity measurements were carried out using a UV–VIS-NIR spectrophotometer Varian Cary 5 equipped with a 110 mm diameter integrating sphere under near normal incidence (3°20') in the wavelength range of 250-2500nm. The reflectivity measurements using linearly polarized light were performed for the parallel (Rp) and perpendicular Rs components of the light vector in the range of 300-2300 nm and at 40, 50, 60 and 70° incident angles with a spectral ellipsometer SENTECH S 850. The XPS measurements were performed under UHV (ultrahigh vacuum) conditions with a VG ESCALAB 210 spectrometer using monochromatized Al Kα radiation ($h\upsilon = 1486.6$ eV) with an energy resolution better than 0.5eV. The binding energy scale was calibrated using the $Au4f_{7/2}$ line of a cleaned gold sample at 84.0eV. Moreover, large scale XPS-spectra from 0 to 1200eV were performed to identify all the elements that the deposited films contained. The acquisition mode was set to CAE (constant analyser energy) with a 20 eV pass energy (0.025eV step size) and normal electron escape angle. Fitting of the core level lines was performed using Doniach-Sunjic functions, after a Shirley background subtraction, using UNIFIT for Windows (Version 2011) software. The convolution of Lorentzian and Gaussian line shapes was used to fit the individual peaks. Then, the intensities were estimated by calculating the integral of each peak; the atomic concentrations were then derived using Scofield sensitivity factors. All the experimental conditions for SIMS and Nuclear Reaction Analysis (NRA) are described elsewhere [5]. The JET plasma operation was 45 h exposure including 32.7h of X-point plasma. The temperature of the mirrors in outer wall was in the range 200-280°C.

3. RESULTS AND DISCUSSION

The investigated mirrors were located in a cassette at different distance from the channel mouth: from 0 to 4.5 cm in the main chamber wall of JET. Detailed information regarding the construction and location of the mirror carriers has been given earlier [3, 5]. Mirrors which were placed near the beryllium evaporator where protected by a magnetic shutter which was open only in the presence of the magnetic field. The shutter protected mirrors located in positions 0 and 1.5 cm. The specular reflectivity of the mirrors exposed in 2008-2009 on the outer wall of the main chamber is plotted in Figure 1. The diffuse reflectivity measured for the 3 exposed mirrors is at the bottom of the graph, mostly below 7% in the visible range for all the mirrors. The decrease in the reflectivity was seen on the Rs and Rp reflectivity. The Rp reflectivity of the Rh mirror before and after JET exposure is plotted in Figure 2. Even though Rh and Mo mirrors have a different initial reflectivity, after exposure similar results were observed. To understand this phenomenon surface analysis was

performed on these mirrors. Figure 3 shows SIMS depth profiles of several isotopes, extracted from the measurements of Mo (top panel) and Rh (down panel) mirrors. As it was fully described in our previous work [5], the Rh coating survived the JET campaign. On the surface one can observe Be and C originating from the JET wall, and also Ni and Mo from the Inconel 625 alloy constituting the JET vacuum vessel (8-10 wt% Mo, 58 wt% Ni, 20-23 wt% Cr, 5 wt% Fe and 3-4 wt% Nb + Ta). Even though these results are only qualitative, we can clearly observe the deposits showing different thicknesses on the two mirrors. SIMS depth profiling (not shown here) was also carried out on the Mo mirrors located at 4.5 cm and the film had a thickness of ~ 1.9 μm and contained mainly Be, C and D in the deposition area (see Micrographs Figure 1a, position 4.5 of reference [5]). The C concentrations measured by NRA were 8.2×10^{16}, 1.4×10^{17}, 6.3×10^{18} at/cm^2 for mirrors located at 0, 1.5 and 4.5 cm, respectively (Figure 6b of reference [5]). More carbon was observed on surfaces located further away from channel mouth. According to SIMS and NRA results the film on the surface is mostly composed of carbon. Core level XPS spectra of the Mo and Rh mirrors as received and after removing a part of the film by etching with Ar^+ ions (2.5keV) are presented in Figures 4 and 5, respectively. On the as-received Mo mirror only Mo, C and O were detected. The atomic concentrations (at.%) are given in Table 1. By XPS the chemical bonding of each element can be determined. The C1s core level spectra revealed three components assigned to carbide, amorphous carbon and C = O at 283.3, 285.7 and 289.1eV, respectively. Mo3d core level spectra correspond to Mo_2C and MoO_3 at 228.4 and 232.6eV, respectively. The O1s was deconvoluted in oxide, water and OH components (not shown here). After 50 min of sputtering the amount of amorphous carbon was drastically reduced and the Mo was fully in a carbide state (Figure 4). The calculated stoichiometry based on the at.% of each component corresponds to Mo_2C. Also, the decrease of the reflectivity in all the measured wavelength ranges is typical for carbide on a molybdenum surface [12] and not only for an amorphous carbon or a molybdenum oxide film [13]. On the as-received Rh mirror, carbon was mostly in an amorphous state (Table 1). A small amount of Rh, Mo, and Fe was revealed by XPS and all elements were in oxide states (Figure 5). Be1s core level spectra revealed one component at 113.4eV typical for BeO or $BeMoO_4$ [14]. The peak at 111eV in the Be1s spectrum was Ni3s signal and was not taken into account in the calculations. Mo was also mostly oxidised and Rh was deconvoluted in RhO_2 and sub-stoichiometric oxide [15]. The Fe2p core level deconvoluted in 2 components (as received) corresponded to a Fe/Ni alloy [16] and Fe_3O_4. After 50min of sputtering Rh had only one component corresponding to the sub-stoichiometric oxide, whereas Mo was mostly in a carbide state. For the Fe2p core level, FeO appeared at 709.8eV. An additional 50min of sputtering was performed for this sample and the wide range scan revealed no further change i.e after 100min of sputtering the substrate was not visible. XPS was also carried out on for an as-received sample located at 4.5cm. The composition measured is given for the region with a thick coating and a shiny part. In both areas carbon was mostly amorphous and all metals were in oxidised states. As seen on the other mirrors, even on the shiny part, the surface was covered with amorphous carbon and a large amount of Be. The SEM images of the Rh mirror

are presented in Figure 6 before exposure a) and after exposure b). The nanometer-size crystallites were visible after exposure and bigger particles were also present on the surface. The different shape of the crystallites is maybe due to a deposited film on top of Rh. For Mo mirror even though the grains were not visible after exposure a large relief pattern was seen on the surface after exposure d) in comparison to before c). This might be an explanation for the high diffuse reflectivity of this sample (Figure 1). For the other mirror micrometer-size particles were also present. This indicated that the use of polycrystalline mirror was not suitable.

SIMS and XPS measurements presented in this paper are in a good agreement and they help the interpretation of reflectivity data. On all the mirrors a film containing amorphous carbon, oxygen and metal like such as Be, Fe, Ni, Mo and Rh in an oxidised state were measured. The thickness of the films varied from a few nm to 2μm depending on the location in the cassette. A higher thickness of a deposited film on Rh mirror located at 1.5cm in comparison to the Mo mirror (0cm) lead to the same reflectivity. Even after Ar sputtering, the Mo mirror was fully carbidised, whereas Rh does not form carbide [17]. The temperature of the mirrors in outer wall was in the range 200-280°C, in which carbon could easily diffuse in Mo to form Mo_2C. This point is really important as the FM in ITER will have to be cleaned in-situ (without breaking the vacuum) either by plasma or by laser cleaning. Moreover, the deposited film on Mo will have to be removed together with the carbide layer, supposing the configuration of ITER divertor with tiles made of carbon fibre composites [18].

CONCLUSIONS

Mo and Rh-coated mirrors exposed in the main chamber wall of JET were characterized by SIMS, XPS, SEM and optical methods. XPS and SIMS measurements were in a good agreement for the deposited films. XPS revealed that the film was mostly composed of amorphous carbon mixed with Be and elements from the Inconel vacuum vessel of JET. Almost all the metal elements were oxidised on the surface. After removing a part of the film by sputtering with Ar^+ ions, a Mo_2C state was revealed on the Mo mirror. The measured reflectivity on the Mo mirror, located at 0cm, showed the influence of the thickness of the deposited film on the optical properties: a thin film on the Mo mirror (estimated by SIMS) results in an identical decrease of reflectivity as is the case for a Rh mirror located at 1.5cm. As the FM in ITER will have to be cleaned in-situ either by plasma cleaning or by laser cleaning, the formation of a Mo carbide on a Mo mirror is really critical. Even if the deposited film is removed by a cleaning technique, the carbide could always be on the surface and will affect the reflectivity. Rh-coated and Mo mirrors are installed in JET for the ITER-Like Wall in order test mirror performance during plasma operation with a full metal wall.

ACKNOWLEDGEMENTS

This work was supported by EURATOM and carried out within the framework of the European Fusion Development Agreement. The views and opinions expressed herein do not necessarily reflect those of the European Commission. The authors would like to thank the Swiss Federal Office of

Energy and the Federal Office for Education and Science for their financial support. This work was also supported by the Swiss National Foundation (SNF) and the National Center of Competence in Research on Nanoscale Science (NCCR-Nano).

References

[1]. V. Voitsenya et al., Review of Scientific Instruments 72 (2001) 475.
[2]. A. Litnovsky et al., Nuclear Fusion. **47** (2007) 833.
[3]. M. J. Rubel et al., Review of Scientific Instruments **77** (2006) 063501.
[4]. M. Rubel et al., Journal of Nuclear Materials **390-391** (2009) 1066.
[5]. M. Rubel et al., Physica Scripta, **T145** (2011) 014070.
[6]. L. Marot et al., Review of Scientific Instruments **78** (2007) 103507.
[7]. A. Bardamid et al., Vacuum **58** (2000) 10.
[8]. A. Litnovsky et al., Nuclear Fusion **49** (2009)075014
[9]. L. Marot et al., Surface and Coatings Technology **202** (2008) 2837.
[10]. M. Joanny et al., IEEE Transactions on Plasma Science, **40** (2012) 692.
[11]. E. Mukhin et al., Nuclear Fusion. **49** (2009) 085032.
[12]. G. De Temmerman et al., Journal of Nuclear Materials **337-339** (2005) 956.
[13]. A. Litnovsky et al., Fusion Engineering and Design **83** (2008) 79.
[14]. V.V. Atuchin et al., Materials Characteristics **59** (2008) 1329.
[15]. L. Marot et al Surface Science **602** (2008) 3375.
[16]. K. Kishi et al., Journal of Electron Spectroscopy and Related Phenomena **46** (1988) 237.
[17]. L. Marot et al., Journal of Nuclear Materials, **390-391** (2009) 1135.
[18]. R.A. Pitts et al., "A full tungsten divertor for ITER: physics issues and design status", 20th PSI conference

	O	C	Be	Rh	Mo	Fe	Ni	N
0 cm (Mo)	27.8	59.0			13.2			
0 cm (Mo) + **50 min Ar^+**	16.8	31.8			51.4			
1.5 cm (Rh)	31.6	50.5	14.7	1.6	0.8	0.8		
1.5 cm (Rh) + **50 min Ar^+**	41.7	17.4	20.7	2.9	2.1	8.6	2.1	4.6
4.5 cm **Shiny part** (Mo)	33.9	37.8	25.5		0.2	0.5		2.1
4.5 cm **Deposited part** (Mo)	28.3	59.0	7.9		0.4	2.4	0.6	1.4

Table 1: Atomic concentrations calculated from the XPS measurements on the mirrors located at 0 and 1.5 cm as received and after 50 min sputtering with Ar^+ ions. Measurements for the as-received mirror at 4.5 cm were made on shiny and areas with deposits.

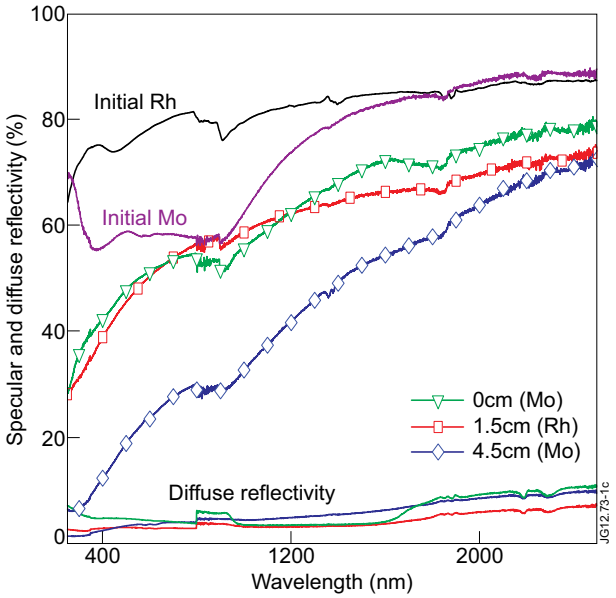

Figure 1: Specular and diffuse reflectivity of the mirrors located at 0, 1.5 and 4.5cm, in black and purple are the initial specular reflectivity measured after Rh coating and on a polished Mo mirror, respectively. The diffuse reflectivity of the 3 mirrors is on the bottom, the same colour coding is used as for the specular reflectivity.

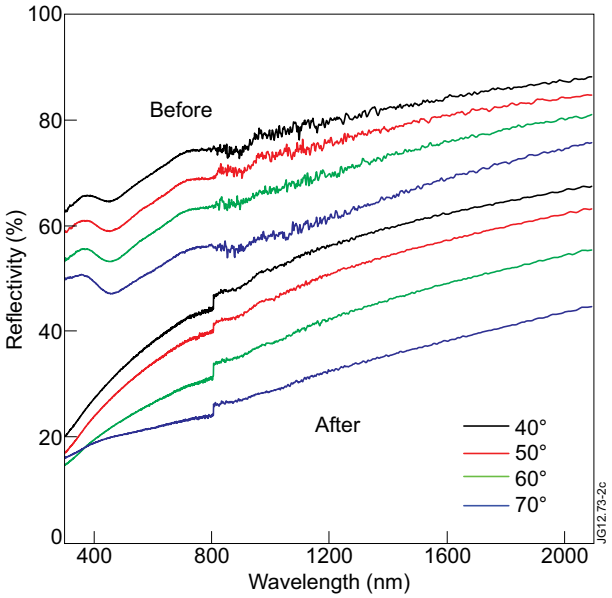

Figure 2: Rhodium reflectivities at 40°, 50°, 60°and 70° for p polarization before and after JET exposure.

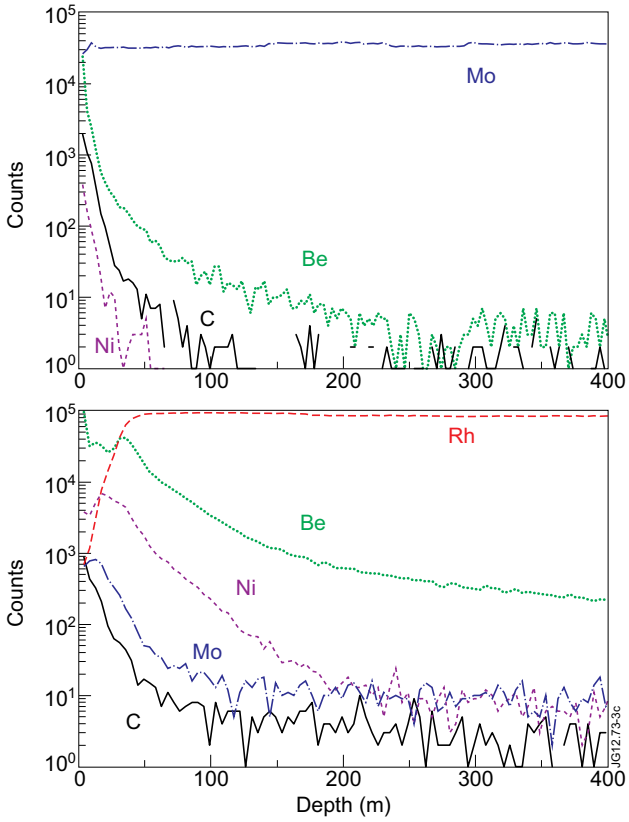

Figure 3: SIMS depth profiles measured on mirrors located at 0 cm (top panel) and at 1.5cm (down panel).

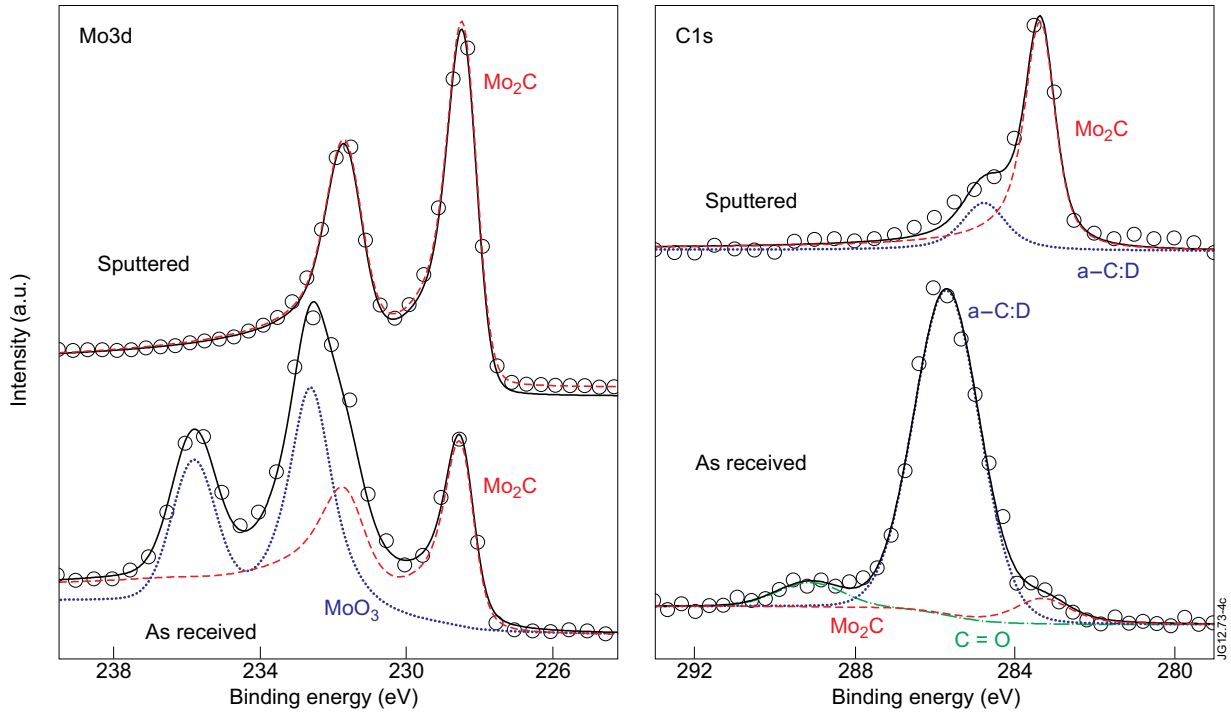

Figure 4: Mo3d and C1s core level spectra of the Mo mirror located at 0cm measured by XPS. All spectra have been normalized for comparison. Open circles are the measured data and full lines are mathematical fits. The coloured curves correspond to the different components, the black one to the fit sum. In case the black line is not visible, it is due to the overlapping of component curve.

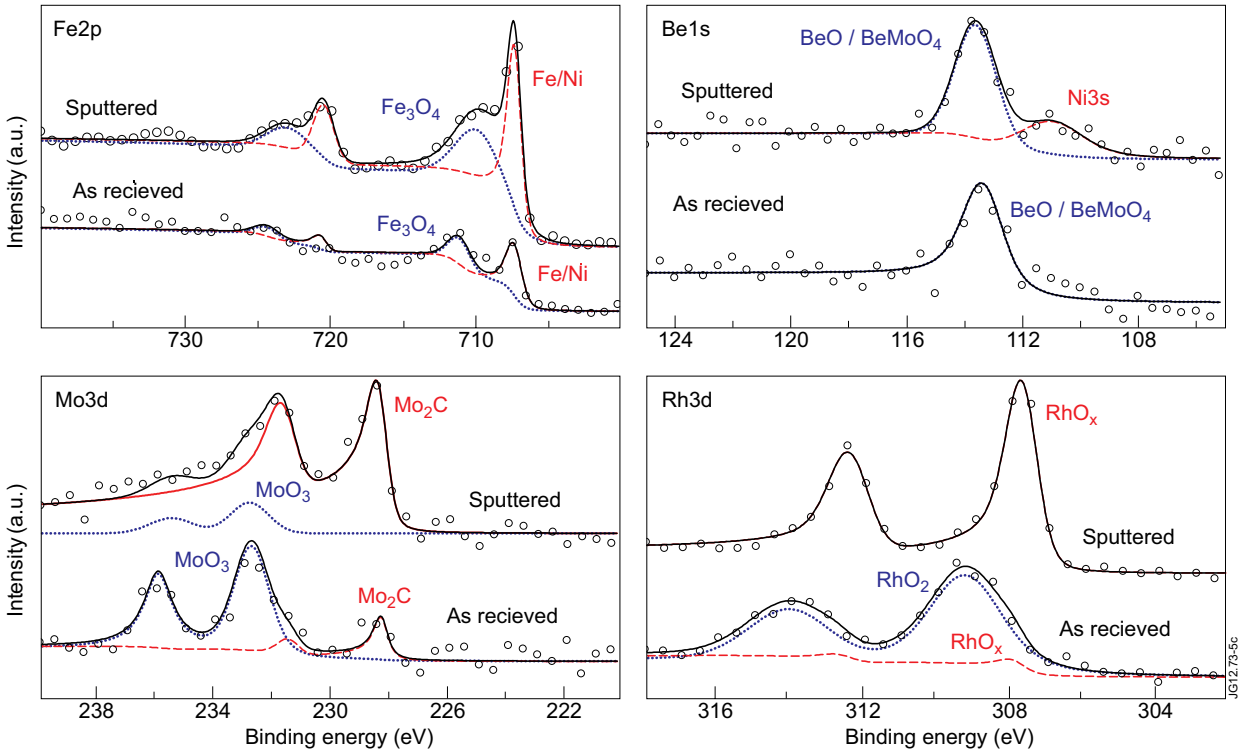

Figure 5: Core level spectra of the Rh mirror located at 1.5 cm measured by XPS. All spectra have been normalized for comparison. Open circles are the measured data and full lines are mathematical fits. The coloured curves correspond to the different components, the black one to the fit sum. In case the black line is not visible, it is due to the overlapping of component curve.

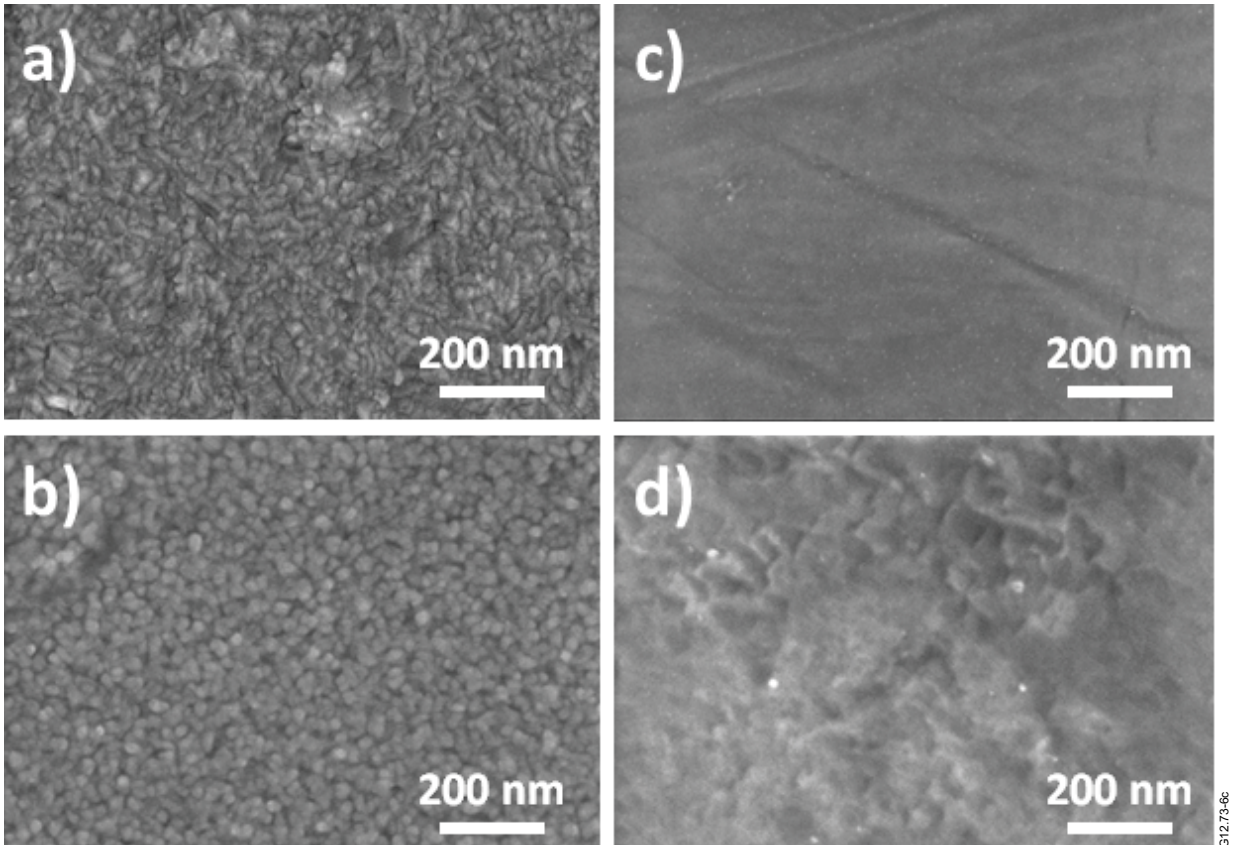

Figure 6: SEM images of the Rh mirror before exposure a), and after exposure b); Mo mirror before exposure c) and after exposure d).