Nanostructured rhodium films produced by pulsed laser deposition for nuclear fusion applications

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ABSTRACT

In this paper the possibilities offered by pulsed laser deposition (PLD) for the production of nanostructured rhodium films with improved properties are explored. Thanks to its high reflectivity and low sputtering yield, rhodium is one of the best candidates for the development of thin films to be used in first mirrors, which are crucial components in many diagnostic systems of thermonuclear magnetic fusion machines, like tokamaks. Due to the features of PLD, by varying the process parameters it is possible to tailor both the structure, i.e. the nanocrystalline domain size of the deposited films, down to less than 5 nm and separately control the other relevant physical properties. This leads to modifications in growth regime and annealing dynamics, in such a way that both morphology and reflectivity achieve the properties demanded to use these films as mirrors for fusion applications, opening at the same time new possibilities for the future improvement of thermo-mechanical and adhesion properties.

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1. Introduction

The fabrication of nanostructured/amorphous metallic films with structural properties different from the corresponding crystalline materials represents a research area of continuously increasing interest [1]. The main reason is that, thanks to their different structure, the deposited films can potentially achieve new properties, such as higher mechanical resistance, better adhesion, higher fatigue strength and better resistance to corrosion, at the same time maintaining other desired properties characteristic of a metal [1,2].

In particular the challenge of producing metallic films with high reflectivity on a wide wavelength range (200–1000 nm) and improved thermo-mechanical and resistance properties needs to be faced for the fabrication of mirrors working in a harsh environment. This is the case of the so called first mirrors which are used in many diagnostic systems of thermonuclear magnetic fusion machines, like tokamaks [3]. These mirrors are placed either at the level of the first wall (retroreflectors), or in properly designed ducts. In any case, these devices are subjected to erosion by sputtering and/or redeposition, high thermal load and neutron flux. It is definitely of fundamental interest to enhance the thermo-mechanical

properties of such surfaces. For this reason, in this field of research the development of mirrors with a controlled structure (single crystal or amorphous) is one of the key issues [5,4].

Thanks to its high reflectivity and low sputtering yield rhodium (with molybdenum and tungsten) is one of the best candidates for the development of mirror thin films [6,7]. Rhodium metallic films have been deposited by electrochemical deposition [8] and magnetron sputtering [9,10]. So far with these techniques it has not been possible to properly control the structure of the deposited films and achieve at the same time a satisfactory reflectivity behavior at high temperature.

In this paper the possibilities offered by pulsed laser deposition (PLD) for the production of rhodium films are explored. PLD is one of the well-known vapor phase deposition processes for fabricating ceramic and metallic thin films. It differs from other deposition techniques, such as sputtering or evaporation, in two main features [11,12]: (i) the higher energy of the ejected species (ions in the keV range and neutral atoms with energies of several eV); (ii) higher instantaneous deposition rates (several $k\text{Å}\,s^{-1}$) which favor non-equilibrium film formation [13]. Thanks to these features amorphous films of Ir and Fe have been obtained during deposition in vacuum [14,15], but no attempts have been made to understand structure modifications with process parameters. Varying laser fluence, background pressure, target-to-substrate distance it is possible to tune the energy of the species and determine the resulting structure and morphology of the growing film [16].

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2. Experimental

In our experiments a nanosecond laser pulse (λ = 266 nm, pulse duration 5–7 ns repetition rate 10 Hz) is focused on a 1 in. Rhodium target (purity 99.9%). The species ablated from the target expand in a proper vacuum chamber and are collected on a substrate, silicon (100) or tantalum, 60 mm far from the target at room temperature. We have changed laser fluence (1.2 or 4.5 J/cm^2) and He pressure (between 6×10^{-3} and 30 Pa) in order to explore the possibility of tailoring the structure of the Rh films without affecting the main features influencing their reflectivity, namely roughness and morphology. The deposited thicknesses have been 200, 500 and 1000 nm, with a deposition rate of 10 nm/min.

The films have been characterized with X-ray diffraction (XRD) using a Panalytical X'Pert PRO X-ray diffractometer in $\theta/2\theta$ configuration, atomic force microscopy (AFM) performed in noncontact mode scanning areas with size of 3–15 µm, scanning electron microscopy (SEM) with a Zeiss Supra 40 field emission SEM (accelerating voltage 3–5 kV) and Ellipsometry using an ellipsometer (J.A. Wollam Co. VASE Ellipsometer) with a working spectral range between λ = 260 nm and λ = 1700 nm.

3. Results and discussion

In Fig. 1 the XRD spectra of the samples produced with laser fluence of 1.2 J/cm^2, thickness of 200 nm and background pressure ranging from vacuum to 30 Pa are shown. The film deposited in vacuum is crystalline; all diffraction peaks are present and there is a preferential growth on the (111) direction, the crystalline dimension, calculated by Scherrer formula, being 15–20 nm. At 2 Pa only the (111) peak is visible, with very low intensity, while the crystalline dimensions are about 7–10 nm. In films deposited with a background pressure higher than 2 Pa, only a weak broad peak in the region of the (111) reflection can be appreciated. In order to understand the role of the different parameters we considered a higher value of fluence, 4.5 J/cm^2, that provides a higher energy of the ablated species, with a background pressure of 15 Pa. As shown in the inset of Fig. 1, with such higher fluence the film returns crystalline. This confirms that film crystallinity is related to the energy of the deposited species. Therefore varying both/either gas pressure and/or laser fluence it is possible to influence the nanostructure of the deposited films, possibly approaching the amorphous state. We have chosen to change only the
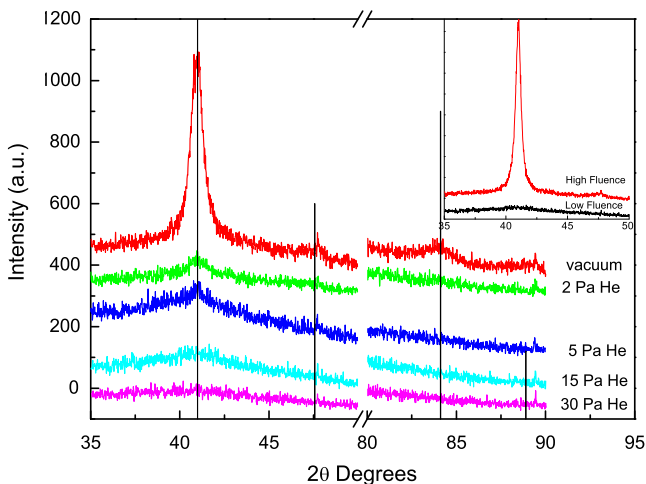
pressure and set the fluence to the lower value in order to minimize droplet formation, a typical drawback of PLD.

Mirror roughness is very important because it is directly related to reflectivity via the Bennet's formula:

$$R = R_0 \cdot \exp\left[\frac{-4\pi r^2}{\lambda^2}\right]$$

where R is the surface reflectivity, R_0 its value at zero roughness, r its roughness and λ the wavelength of the considered electromagnetic wave. Roughness has been measured using AFM, calculating the root mean square of the profile. Changing the deposition pressure from 6×10^{-3} to 15 Pa, the corresponding roughness increases from 0.39 to 0.89 nm, respectively. The deposited films are thus very smooth; even at the highest considered pressure the roughness is less than 1 nm. Since the roughness of the Si substrate is about 0.1 nm we conclude that the chosen deposition energy is high enough to ensure the deposition of smooth and compact films in which the roughness does not significantly increase with respect to the substrate one.

We have deposited thicker films (500 nm and 1 µm), in order to investigate more realistic values for a mirror. The XRD analysis, shown in Fig. 2, reports a change in the crystallinity, that is related to the thickness via the columnar growth [13]. The crystalline dimensions grow from 12 nm (thickness 200 nm) to 24 nm (thickness 1 µm) for the film deposited in vacuum, from 7 to 15 nm for the samples deposited at 2 Pa while they do not change with the deposited thickness at higher pressures, always remaining well below 5 nm. This confirms the existence of an energetic regime that leads to the deposition of nanocrystalline films even at high values of thickness.

Fig. 3a and b refers to SEM cross sections images of 500 nm films deposited at 2 Pa and 15 Pa, respectively. The film deposited at lower pressure is characterized by close packed crystalline columns while, on the contrary, the film deposited at higher pressure shows a morphology characterized by nanocrystalline grains in a non-columnar order. On the plain view both films appear very smooth, with roughness of the same order of the thinner films, although we note the presence of some small droplets. More specifically, the crystalline domains constituting the film are clearly visible in the lower pressure case (Fig. 3c), contrary to what happens in the higher pressure case (Fig. 3d), where they are too small to be detected with SEM.

Some of the thicker films deposited in vacuum on the Si substrate present sub-millimetric corrugations that greatly degrade film specular reflectivity. This phenomenon is called buckling and is related to the relaxation of the compressive stresses that are present in the film [17]. If the deposition pressure is increased, the samples are less subjected to buckling and at 15 Pa the film returns completely smooth. We can therefore conclude that by tuning the energy of the ablated species it is also possible to influence and control the amount of residual stress.

In order to understand the role of the substrate we deposited the films on Ta that is similar to the substrates for realistic first mirrors, Mo and W. Thanks to the different nature of the substrate and its higher roughness, more than 50 nm, we obtained perfect adhesion of the films for every deposition pressure and thickness, without further increasing the overall mirror roughness with respect to the substrate value. This suggest that, by choosing a proper compromise for the value of the substrate roughness, it is possible to obtain a satisfactory adhesion without substantially interfering with the smoothness of the deposited film.

The thermal behavior of the deposited films has been tested annealing the samples in vacuum at 200 and 400 °C for 6 h. 200 °C is the normal operation temperature for this kind of devices inside tokamaks [18,8], while 400 °C is the temperature
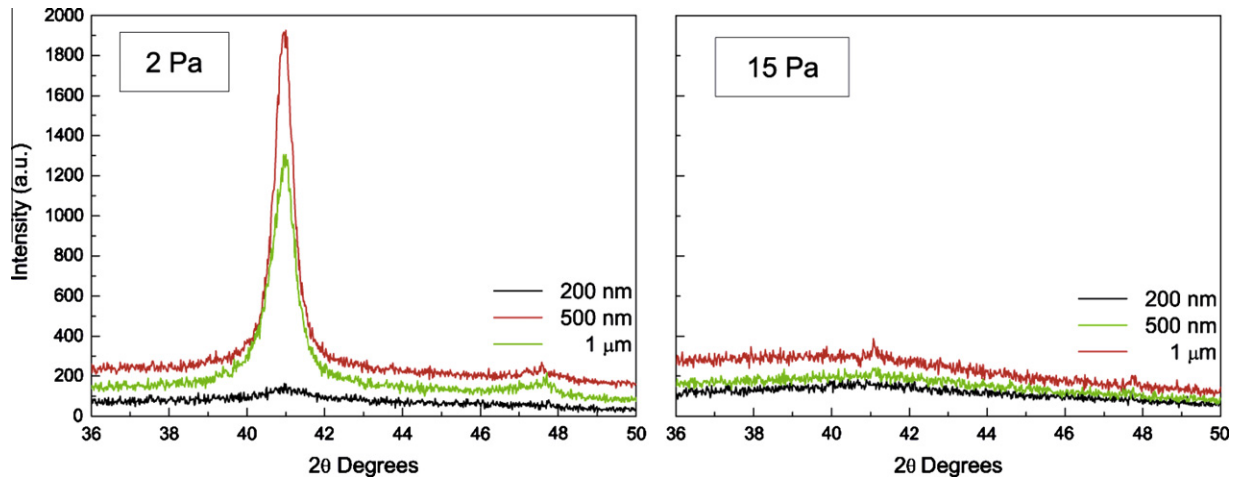

Fig. 1. XRD spectrum of rhodium film varying He background pressure from vacuum to 30 Pa, inset: depositions made at 15 Pa at low (1.2 J/cm^2) and high (4.5 J/cm^2) fluence.

Fig. 2. XRD of Rh films with different thickness deposited at 2 and 15 Pa, respectively.
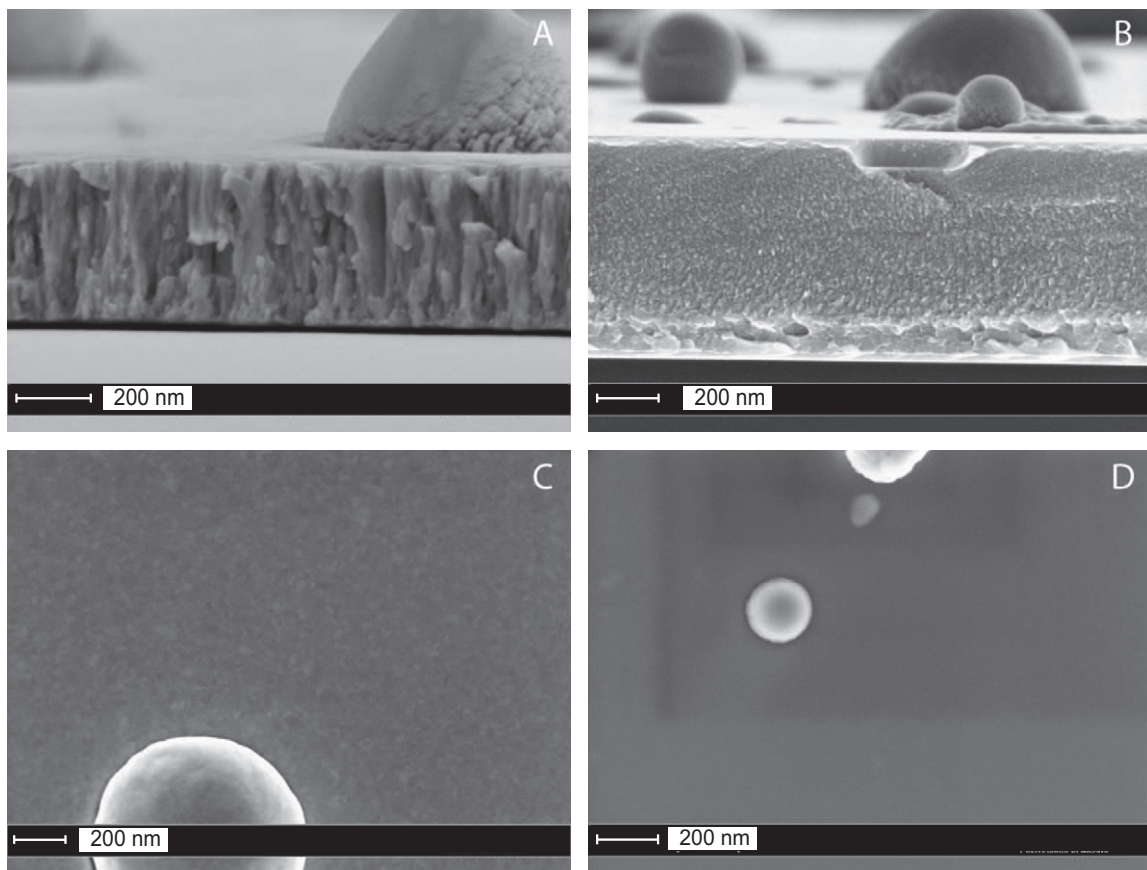

Fig. 3. SEM cross section and plain view of Rh films deposited at 2 Pa (a and c) and 15 Pa (b and d), respectively; the different growth regime is clearly visible.

reached during a typical cleaning operation (glow discharge). The annealed samples have been characterized by SEM and XRD. At 200 °C there are no relevant changes in morphology and structure of the films. At 400 °C we have the formation of crystalline domains for all the deposited samples depending on the deposition pressure, see Fig. 4. This behavior can be qualitatively interpreted considering that the bulk Rh re-crystallization temperature should be 470 °C (if calculated as one third of the melting absolute temperature), but may be even lower in our case considering the long annealing time and the high degree of disorder of the deposited film. In Fig. 4a and b the film deposited in vacuum before and after annealing is shown: a growth of crystalline domains (50–200 nm) is observed. For the samples deposited at intermediate pressure, 2–5 Pa, Fig. 4c and d, we have the presence of either large crystalline grains (hundreds of nm) or small nanometric crystals. For samples deposited at 15 Pa, Fig. 4e and f, the film is constituted only of 34 nm nanocrystals, as measured by XRD (not shown). Therefore the structure of the deposited film greatly influences the dimension of the crystalline domains after annealing.
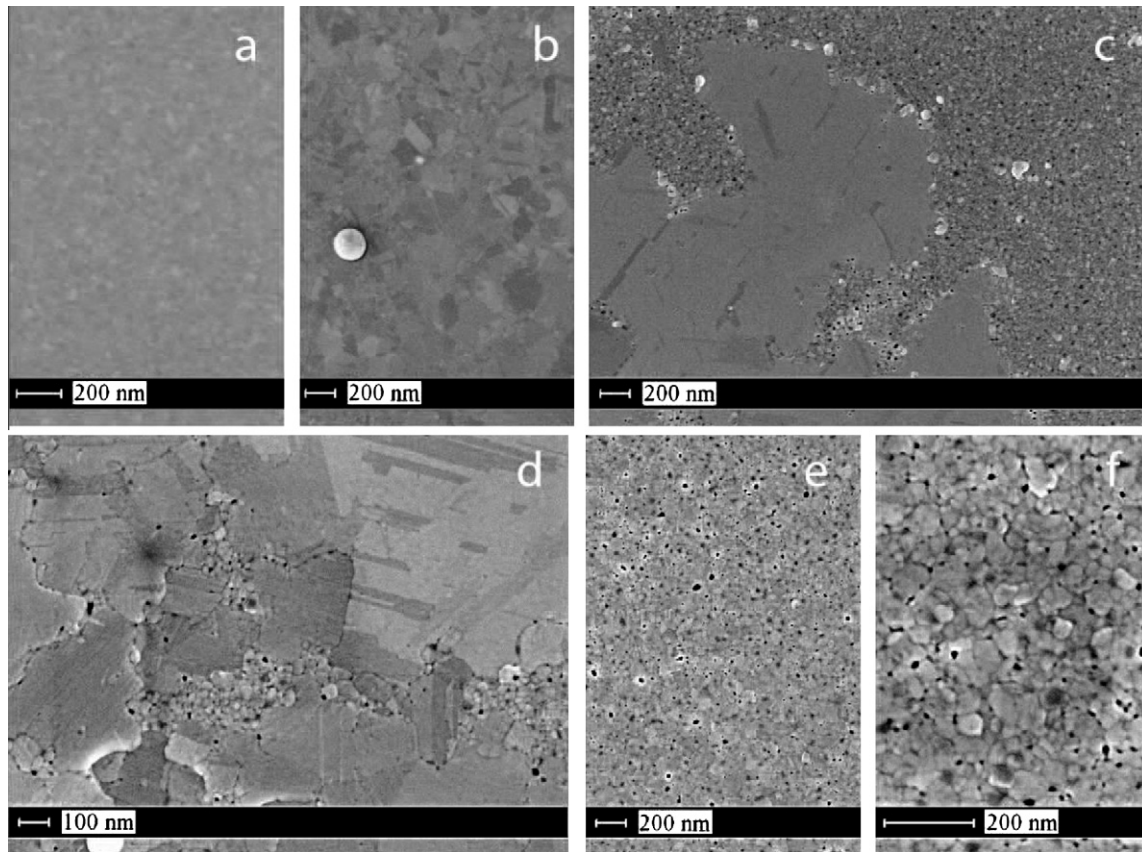
Fig. 4. (a) SEM of Rh films deposited at 6×10^{-3} Pa (not annealed). Films annealed at 400 °C for 6 h and deposited at 6×10^{-3} Pa (b), 2 Pa (c), 5 Pa (d) and 15 Pa (e and f).
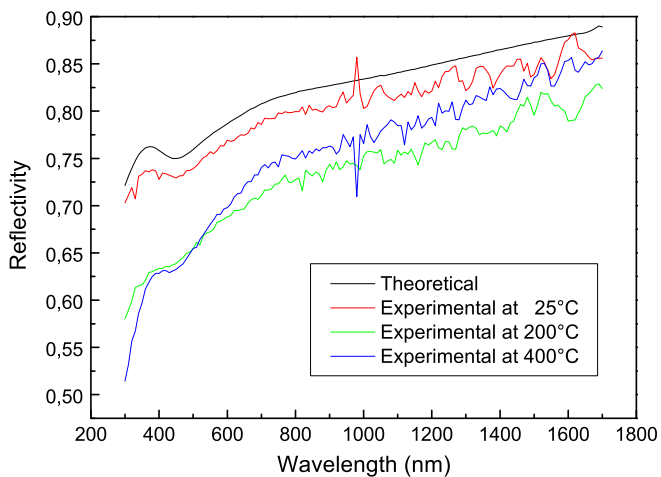

Fig. 5. Specular reflectivity spectra of: (i) a calculated reference [19], (ii) the Rh film deposited at 15 Pa and the same sample annealed at (iii) 200 °C and (iv) 400 °C.

We then checked the reflectivity of our deposited films. In Fig. 5 the specular reflectivity spectra of: (i) a reference calculated using the optical constants of bulk rhodium [19], (ii) a film deposited at 15 Pa, (iii) the same film annealed at 200 °C and (iv) at 400 °C are reported. The non-annealed film exhibits a reflectivity that is comparable with the reference: the slight difference can be related to a scattering effect due to droplet formation induced by the deposition process. All the films deposited varying the pressure present the same reflectivity in spite of the previously described large variations of the structure. This is possible thanks to the high energy regime allowed with PLD, while it is much more difficult to achieve this flexibility in separately controlling the various physical properties with other deposition techniques, in which it has been actually observed that a slight variation of the process parameters (e.g. pressure in sputtering deposition) causes a dramatic decrease of reflectivity, until 40% [10]. When the film is annealed, even at 200 °C we note a non-negligible reduction in reflectivity, of about 20%, especially at the short wavelengths, which could be related to the presence of a roughness due to annealing or the presence of voids in the surface that modify the effective refractive index of the film [10].

4. Conclusions

In conclusion we have deposited rhodium thin films to be used for diagnostic mirrors. We have shown that, exploiting the features of the PLD process, it is possible to modify the structure of the deposited film approaching the amorphous regime without affecting the morphology. On the basis of these findings, the path for the production of films with improved thermo-mechanical and adhesion properties, possibly resulting in better overall performances, is open.

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