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Optical and Structural properties of noble metal nanoisLAND

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ABSTRACT

Metallic nanostructures are widely studied because of their peculiar optical properties. They possess characteristic absorbance spectra with a peak due to plasmonic resonance. This feature is directly dependent on the nanostructures shape, size, distribution and environment surrounding them. This makes them good candidates for a variety of applications, such as localized surface plasmon resonance sensing (LSPR), surface-enhanced Raman scattering (SERS) and photovoltaics. A well established technique used to create nanoisland on flat substrates is performing a thermal treatment after the deposition of a thin metal film. While the most widely investigated metal in this context is gold, we have extended our investigation to palladium, which is interesting for sensing applications because it has an excellent hydrogen absorption ability. The morphological properties of the nanoisland depend mainly on the starting thickness of the deposited layer and on the annealing parameters, temperature and duration. The deposition and annealing process has been investigated, and the resulting samples has been tested optically and morphologically in order to optimize the structures in view or their application for sensing purposes.

Keywords: gold nanoparticles, palladium nanoparticles, annealing process, LSPR

1. INTRODUCTION

In the last 20 years there was a great interest on metallic nanostructures including nanofilms and nanoparticles (NPs). These materials present in fact particular properties, which differ from the ones of the bulk materials with the same composition. Moreover, the optical and chemical properties can be tuned by varying their size, shape and distribution. Metallic nanostructure created on transparent substrate present an absorption spectra resonance LSPR depending on the size and morphologic of the nanostructures [1], [2]. This phenomena is correlated with a refractive index changes on the medium surrounding the metal. Therefore, the morphological control and consequent tuning of the optical properties is very important. Metal thin island films, apart from the interest for sensing applications, are studied also for the enhancement of the local electromagnetic field in SERS (surface-enhanced Raman scattering) and infrared spectroscopy [3]. Moreover considering nanostructured made by palladium they are been studied for catalyst, membrane, filters and sensor application [4]. A well establish method to create metal NPs on glass substrate is the immobilization of colloidal monolayer through organic linkage. This method however present a nonuniform distribution of NPs and a very low reproducibility and stability [5]–[8]. From the other side a respectable technique used to create nanoislands on flat substrates, consist to perform a thermal treatment after deposition of a thin metal film [2]. Moreover this technique present advantages like high density of islands, minor agglomeration, cost effectiveness and higher SNR (signal to noise ratio) in biosensing applications [5].

In the case of thermal annealing, a thin film of metal is deposited over a transparent substrate, which will be transformed by an irregular structure of the grains to a more ordered and agglomerate clusters. The transformation of the bulk material to the islands is ruled by the surface energy of each interface [9], [10]. Once that nanostructures are created, an optical and morphological characterization of the film is required. The morphological properties of the film depend mainly on the starting thickness of the deposited layer and on the annealing parameters, temperature and duration. Upon thermal treatment, in fact ultrathin metal films can develop holes and eventually fragment into an array of nanoparticles with a shape resembling a sphere, which minimizes the surface to volume ratio in order to minimize the total energy of

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the system. Although the most widely investigated metal in this context is gold for its chemical stability to various environment, other metals like silver, copper, nickel and palladium were investigated [10], [12]–[14].
Nevertheless this field of application is very studied, for what concern Palladium NPs created with thermal dewetting is scarcely been reported [4]. In particular morphological analysis and optical characterization on thin film palladium nanostructured created with annealing process results very interesting. Palladium thin films result very interesting for its various high-functionalities, such as catalytic activity for many chemical reactions and hydrogen storage and sensing applications [15]. In this work we report a study on NPs for gold and palladium metal created with thermal treatment, characterizing samples both in morphologic analysis and from an optical response.

2. MATERIAL. METHOD AND RESULTS

We divide the experiment in two different part: the first one regarding gold material and the other palladium one. Gold films have been evaporated at 0.5 Å/s on glass (BK7 15 x 15 mm) substrates by electron beam evaporation technique in a chamber with $3 \cdot 10^{-6}$ mbar of pressure.. The substrates have been previously cleaned by ultrasonic bath in isopropyl alcohol. The thickness of Au layer was about 2 nm, measured by a contact profilometer. In order to verify the effects of the annealing process on the morphology and on the optical response of the films, the samples have been heated at different temperatures (200°C, 300°C and 400°C) for 5 minutes. We used a muffle oven with atmospheric pressure inside the camera. Once the samples were annealed at different temperature, they have been analyzed with XE-70 AFM ParkSystem (atomic force microscope) in non-contact mode. In *Table 2* are reported the images and some surface profiles after annealing process. In particular it is possible to see how the structure of gold film change before and after dewetting process assuming a shape very similar to small spheres. After created this structure, it is possible to evaluate the relative volume of the nanoislands and consequently the size and the diameter of the NPs. In fact, in *Table 3* we reported the volume, height and diameter of the NPs coating the film. We notice that the grain size of the heated films is almost double the size of the reference one. The average height also increases; on the other side no big differences are evident between the different temperatures. Another characteristic very important in the case of the Au thin film is the optical response of the samples. In particular the theoretical absorbance peak of gold is situated around 650 nm [11]. In the case in which samples present morphological differences and when the wavelength of the incident radiation is higher than the structure present, we expected a different behavior due to the LSPR (Localized surface plasmon resonance).
The transmittance T of the samples has been measured in the visible range with UV-Vis-NIR Cary 5000 spectrophotomer. In order to verify the absorption due to the resonance it is more convenient to look at the absorbance A, which is defined as

$$A = -log_{10}T$$

In *Figure 1* it is reported the spectra of the samples annealed at three different temperature, 200, 300 and 400°C and the reference one. The main characteristic of the optical response of Au samples is the shift of the absorbance peak both in position and in intensity. Values of interest are reported in *Table 1* and *Figure 1*.

Table 1 Roughness and peak position of Au samples

Temperature [°C]	A_{max} position [nm]	A_{max} value	Roughness [nm]
RT	640	3	0.48
200	562	0.16	2.1
300	546	0.13	2
400	533	0.09	1.5

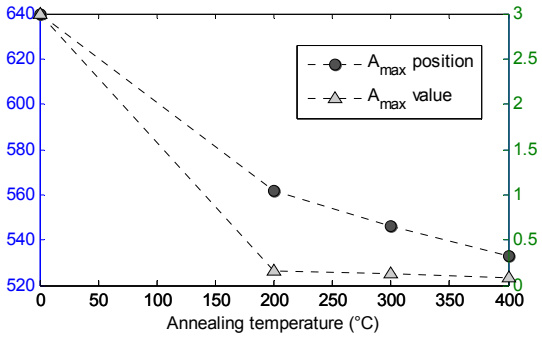


Figure 1 Shift of absorbance peak of Au samples

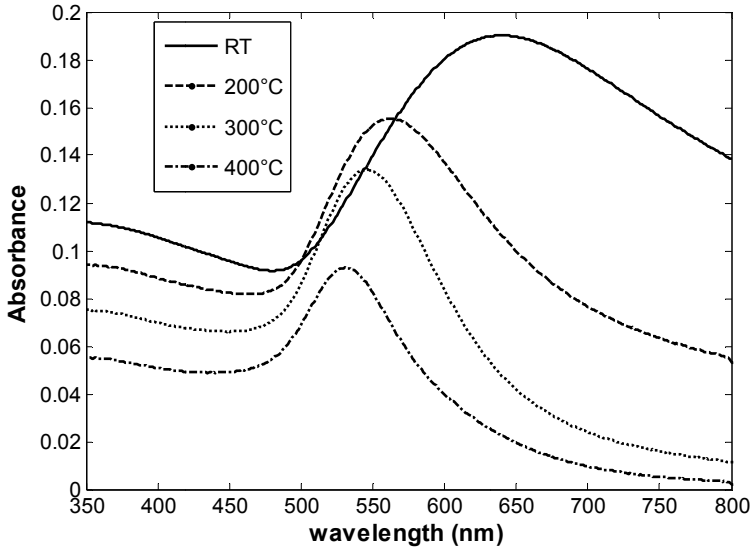
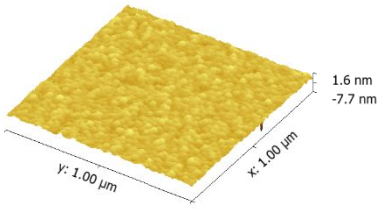
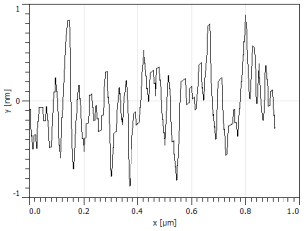
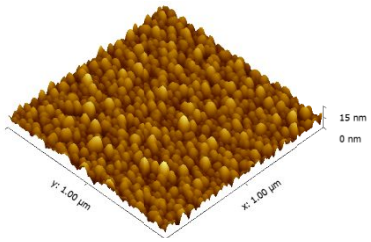
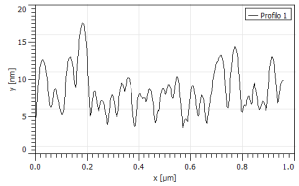
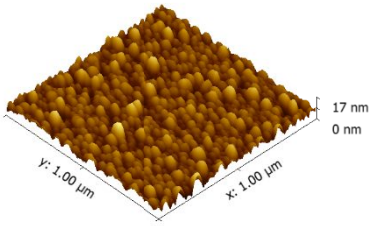
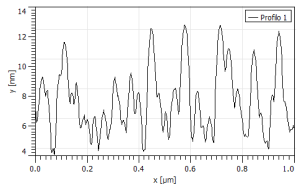
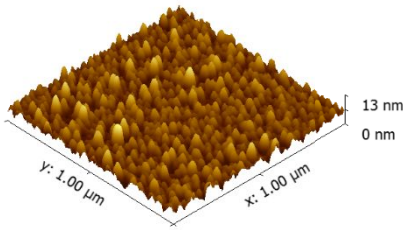


Figure 2 Experimental absorbance spectra after different annealing treatment.

Table 2 AFM images of annealed Au samples

Reference		
200°C, 5 min.:		
300°C, 5 min.:		

400°C, 5 min.:



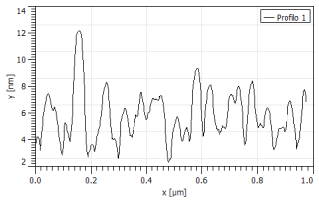


Table 3 Parameter evaluation of NPs

T (°C)	R_{eq} (nm)	Average base section (nm)	Average height (nm)
0	13.4	15	3
200	25.4	30	15
300	25.8	29	13
400	22.2	29	12

Once created and characterized Au NPs, the second part of the experiment regards palladium thin films. Different thickness of Pd films have been evaporated at 0.5 Å/s on Fused-Silica (15 x 15 mm) substrates by electron beam evaporation technique in a chamber witt $6 \cdot 10^{-6}$ mbar of pressure. The substrates have been previously cleaned by ultrasonication bath in isopropyl alcohol. After deposition the various thickness of Pd layers (3,7,10,13,20 nm) were measured by a contact profilometer. Then, the different samples were annealed at various temperature, from 400 to 1000°C: in *Table 4* are reports some data about the sample of 13nm. Once the samples were heated in a tubular oven in vacuum atmosphere ($3 \cdot 10^{-3}$) they were subjected to a controlled descent temperature. The first main difference present in some annealed samples was that a chemical change on the Pd exists; in fact the color of Pd changes between grey/blue to yellow/orange/brown. A picture of the sample *F4* is reported in *Figure 3*. This phenomena was due to the oxidation process of the Pd thin film. It happens by treating the metal with oxygen under the value of 900°C, where the oxide reverts to palladium metal and there isn't oxygen present inside the chamber.

$$2Pd + O_2 \rightarrow 2PdO$$

From literature it is well known that monoxide of Palladium in presence of hydrogen atmosphere returns to Pd metal. In fact, it is possible to see in *Figure 3* a picture of sample F4 before and after hydrogen treatment. For a chemical point of view palladium is a very good receptor of hydrogen and molecules of hydrogen react with oxygen present in the film creating OH basis or water. Then these molecules evaporates at RT leaving a metal thin film of Pd.

$$PdO + H_2 \rightarrow Pd$$

We have exposed this kind of process some of our samples subjecting the PdO films to a flux of 95% of N (nitrogen) and 5 % of hydrogen (H). This operation was made in a non vacuum chamber for 15 minutes.

Table 4 Characteristic of the 13 nm Pd samples

Nome – Sample	Temperature (°C)	Thickness [nm]	Time [min]	Roughthness [nm]	Req [nm]	Roughness after H_2
A4	0	13	0	0.7	25	~~0~~
B4	400	13	30	2.1	29	1.6
F4	600	13	30	4.0	58	2.9
G4	800	13	30	13.4	80	5.7

In *Table 4* are reported the some important parameters of the family X4 samples, both before and after hydrogenation process. In particular, it is possible to see how the estimated radius of the NPs increase considering depending on the thickness of the layer and on the temperature. From the other side if the thickness of starting sample was too thick, no material remains above the glass substrate. Moreover, after the hydrogenation process a decrease on the roughness of the samples is present, reducing the dimension and the volume of NPs. In *Figure 4* it is showed the optical response of the X4 family after annealing process at different temperature. It results very evident that the material over the substrates is changed from palladium, presenting a resonance peak in the visible spectrum. From the other side different response of the samples is due to a diverse morphological structure thus presenting a different LSPR resonance. Nevertheless, the final aim of the experiment was achieved, creating nanostructured of palladium over transparent substrates. This process was demonstrated by the final roughness of the samples and by different optical response reported in *Figure 5*.

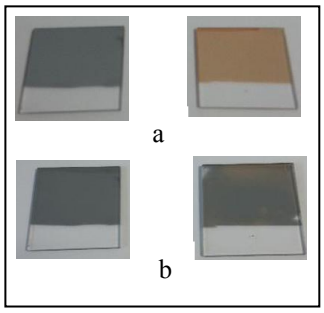
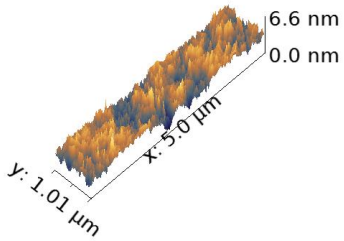
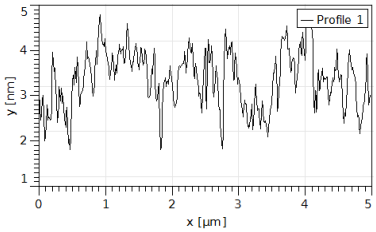
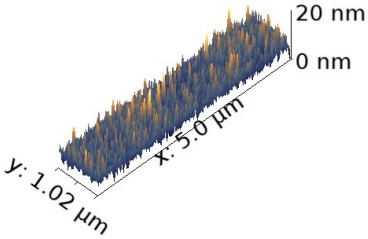
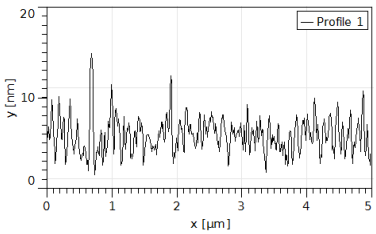
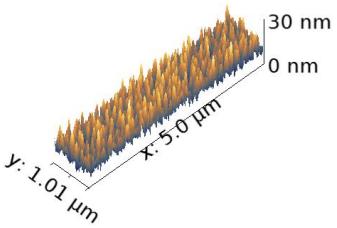


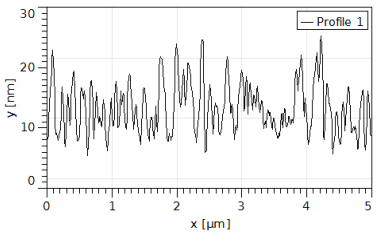
Figure 3 Pd samples after annealing process (a) and after hydrogenation process (b)

Table 5 AFM images of annealed X4 family PdO samples

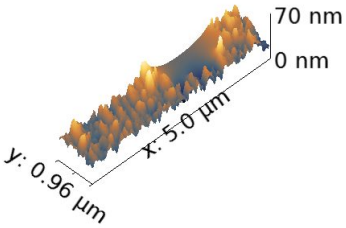
A4		
B4		

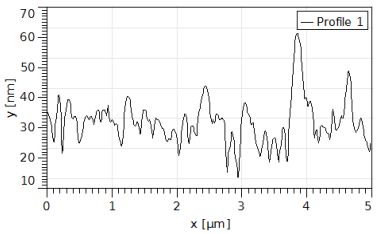
F4





G4





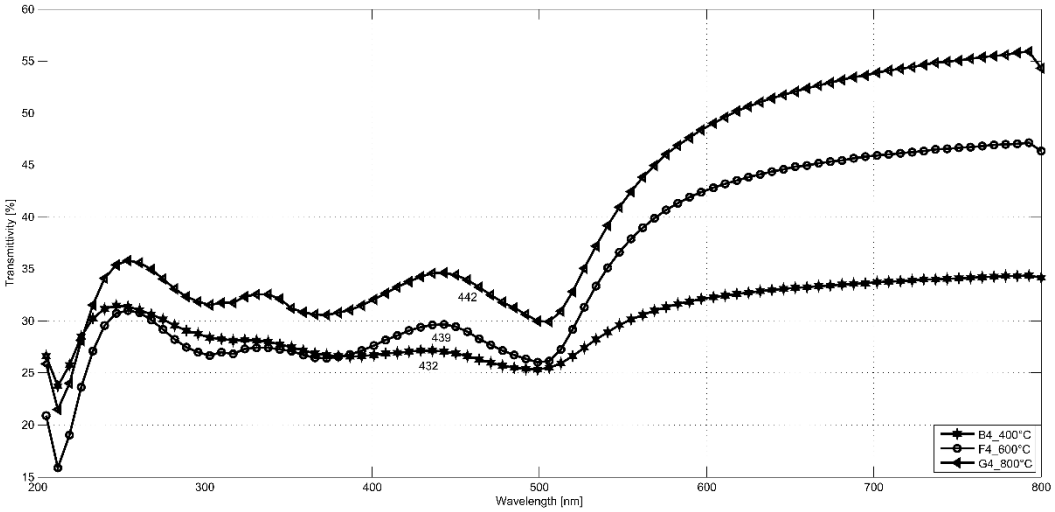


Figure 4 Optical response of 13 nm PdO films.

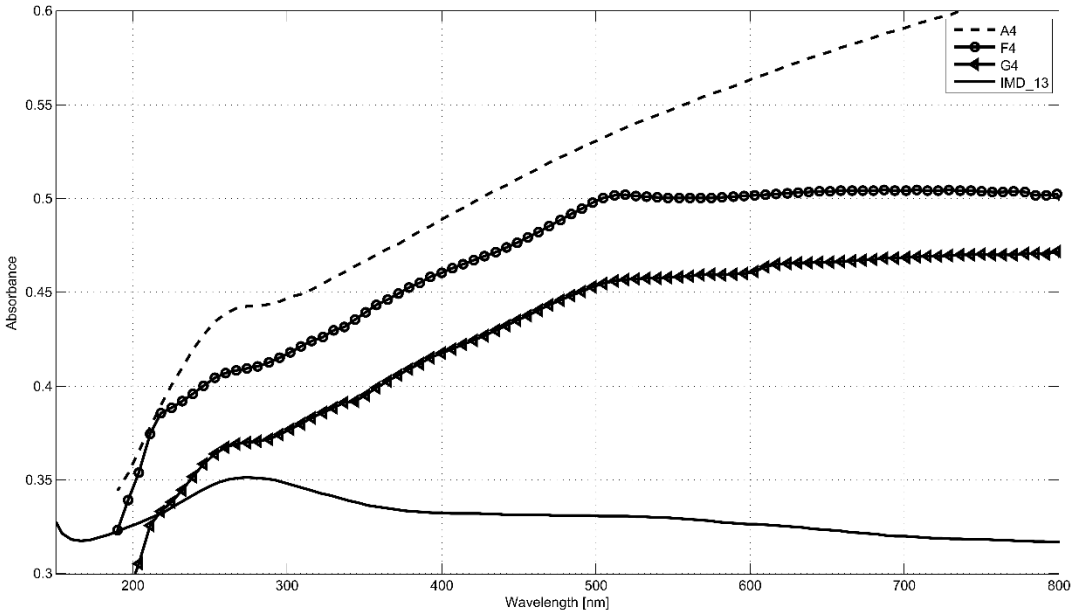


Figure 5 Absorbance spectrum of 13 nm Pd thin film after hydrogenation process

In particular in *Figure 5* it is reported the absorbance of 13 nm family thin films, annealed at different temperature and after hydrogen process. In addition, we present the theoretical absorbance curve of 13 nm of palladium, evaluated with IMD and the response of A4 sample, representing the reference sample for the Pd. It is not easy to define a prediction on the position and on the intensity of the absorbance peak, but a different behavior due to different roughness is present. In any case the behaviour of the PdO respect to Pd after hydrogenation process is completely different both from reference of Pd (A4) and from PdO.

3. CONCLUSIONS

In this work, we investigate two different materials, useful for their optical, chemical and structure characteristics for the creation of metal nanoparticles by annealing process. Thermal dewetting represent an easy, cheap, stable and repeatable method for creating nanostructured based on metal thin layer. In particular, thin films of Au were annealed at different temperature giving rise to various samples with diverse optical and morphological characteristics. It was possible to evaluate the dimension, the height and the total volume of the NPs presented over the substrate. From the other side we considered Palladium for its big properties in a lot of field, chemistry, sensing, etc. In this case, it was more difficult to obtain a stable behavior of the NPs and above all the problem of oxidation was taken into exam. It was demonstrated a LSPR response presented by PdO samples and different optical response of Pd samples after hydrogenation process. Surely further analysis with different techniques like XPS, XRD, SEM, is required in order to better understand the completely response of Pd, but a step toward a very simple method for creating Pd NPs was made.

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