The 26th Iranian Conference on
Optics and Photonics (ICOP 2020),
and the 12th Iranian Conference on
Photonics Engineering and
Technology (ICPET 2020).
Kharazmi University,
Tehran, Iran,
Feb. 4-5, 2020

Kharazmi University

اثر جفت شدگی پلاسمونی در لایه نازک Pd/Au به منظور حسگری گاز هیدروژن

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چکیده- در این مقاله نانوذرات طلا بر روی زیرلایه کوارتز تو سط روش لایه‌نشانی لیزر پالسی در دماهای مختلف لایه‌نشانی شده و سپس کاتالیست پالادیم برای حسگری گاز هیدروژن توسط روش اسپاترینگ بر روی آن قرار گرفته است. طیف UV-Vis، جابجایی پیک پلاسمونی طلا را برای دماهای مختلف لایه نشانی نشان می‌دهد، که ناشی از اثر جفت شدگی پلاسمونی می‌باشد. طیف عبوری نمونه‌ها هنگامی‌که در معرض گاز هیدروژن (۰/۲ تا ۱۰٪) قرار می‌گیرند، بیان کننده این است که نمونه‌ی لایه نشانی شده در دمای اتاق ، جابجایی طول موجی بیشتری را نشان می‌دهد. به طور کلی، نشان داده شد که اثر جفت شدگی پلاسمونی در لایه نازک طلا ، ابزاری مناسب برای حسگری دقیق هیدروژن می‌باشد.

کلید واژه- اثر جفت شدگی پلاسمونی، تشدید پلاسمون سطحی جایگزیده، حسگر هیدروژن، لایه نشانی لیزر پالسی و لایه نازک طلا

Plasmon coupling effect of Pd/Au thin films for sensing hydrogen gas

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Abstract- In this study, nanoislands gold thin films were fabricated by pulsed laser deposition (PLD) method on quartz substrates at different substrate temperatures of 25, 300, 450 and 600 °C. A thin (4-5 nm) Pd film as hydrogen catalyst over-layer was sputter deposited on Au films. UV-Vis spectrometry showed localized surface plasmon resonance (LSPR) absorption shift for RT, 300, 450 and 600 °C substrate temperature. These spectral variations were mainly attributed to the layer morphology based on plasmon-coupling effect. Transmittance spectra at various hydrogen concentration of 0, 0.2, 0.5, 1, 2, 4, 6, 8 and 10% revealed that the layer created at room temperature provides the most spectral shift among other samples. Overall, we showed that plasmonic coupling of PLD derived Au thin films is a suitable tool for accurate detection of hydrogen.

Keywords: Au thin films, pulsed laser deposition, localized surface plasmon resonance, plasmon coupling and hydrogen sensing.

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1. Introduction

Hydrogen is used and generated in chemical, petroleum, glass industries and interested as a renewable, clean and ecofriendly nature energy source because it burns cleanly in air and is non-toxic [1]. Hydrogen is highly flammable and explosive in a wide range (4–75%V), so there is an absolute need to hydrogen sensors for safety point [2]. Different methods for hydrogen sensing have been studied but recently optical hydrogen sensors which based on the phenomena of the localized surface plasmon resonance (LSPR) in metal nanoparticles are more attention [3]. These sensors are very sensitive to the dielectric changes of environment and also decrease the risk of explosion and not be affected by electromagnetic interference, so plasmonic sensors are desirable for industrial applications [4].Gold is the most studied plasmonic material, that show strong plasmon peak in visible light region are chemically stable, but, active sensing materials for absorb hydrogen gas are needed (indirect plasmonic sensing) [5].The Most of hydrogen sensors used palladium, because of its selectivity and ability to absorb hydrogen gas [6]. Gold NPs are not only sensitive to their surrounding refractive index but also they are sensitive to the proximity to other gold NPs of their nearby known as plasmon coupling effect [7]. When LSPR NPs distance is less than their diameter, they coupled together and form a plasmonic absorption with a considerable red-shift. If the separation between particles increases, a blue shift is principally expected [8]. If a thin layer of Pd is deposited on a gold nanoisland layer, the stress resulting from the formation of PdHx (which is even up to several times the initial volume) can be transferred to the coupled gold nanoislands and induce increase in their separation, leading to plasmonic shift. Such an idea can be considered as a new platform for precise hydrogen sensing. The main contribution of this work is to fabricate plasmonic gold nanoisland thin films by PLD method with a sputter deposited thin Pd over-layer and use them as plasmonic hydrogen sensor. Transmittance changes of Au LSPR peak during hydrogen uptake by Pd layer was recorded and the effect of deposition temperature on detecting hydrogen gas was elucidated. Morphological, and optical properties of all Pd/Au samples were investigated by using FE-SEM and UV-Vis spectrophotometer, respectively.

2. Materials and method

2.1. Preparation

Pd/Au thin film are prepared by the pulsed laser deposition (PLD) method and dc sputtering respectively. Gold nanostructure was prepared by PLD method using a KrF excimer laser (248 nm) at a pulse duration of 20 ns and a repetition rate of 10 Hz to ablate a rotating Au target (99.99%, PAMP S.A. Switzerland). The ejected Au nanoparticles are deposited on the quartz substrate (approximately 1×1 cm^2). Experiments are carried out in a vacuum chamber at a pressure of 7×10^{-5} Torr for 180 s in four different temperatures (RT, 300, 450 and 600˚C as labelled S_{RT}, S_{300}, S_{450} and S_{600}). After the gold layer, palladium is deposited by the sputtering method at room temperature. The sputtering deposition was performed using metallic Pd (purity: 99.9%, size: φ = 30mm) target in a pure argon atmosphere for 3 s and its pressure during deposition was $6*10^{-2}$ Torr. The sputtering discharge current and voltage was 5mA and 500V respectively (power = 25W).

2.2. Measurements

The microstructure of the Pd/Au nanoislands deposited on quartz substrate was analyzed with a Field Emission Scanning Electron Microscopy (FE-SEM) using a FEI Quanta 450 field emission microscope. UV–Vis transmission spectra of Pd/Au nanoislands were recorded in a Perkin Elmer Lambda 25 spectrophotometer in 190-1100 nm wavelength range.

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3. Results and Discussion

3.1. UV-Vis

Optical transmission spectra of as-prepared Pd/Au samples deposited at different substrate temperatures are shown in top left panel of Fig.1. The transmittance valleys are due to LSPR absorption of samples, which are located at 732, 606, 586 and 560 nm for RT, 300, 450 and 600 °C substrate temperature, respectively. Sample S_{RT} shows a broad LSPR peak while by increasing the deposition temperature from RT to 600 ° the LSPR peak undergoes a considerable blue shift (Fig.1 down left panel) and become narrower and sharper. These spectral variations are partially attributed to the effect of increasing the substrate temperature to a decrease in particle size as Fig.1 indicates [9]. However, more importantly, the layer morphology as is discussed in the following has a predominant effect on this blue shift. To investigate better plasmon coupling effect, binary images of the samples were prepared using ImageJ software (shown in right panel of Fig.1). For room temperature, the Au NPs are very close together and by increasing the temperature to 600 °C, they are separated so that single spherical NPs are forming over the surface. The considerable red-shift is attributed to decrease in coupling strength of NPs [10]. After hydrogen exposure to Pd/Au films, the Pd layer volume increases and induced a surface tension leading to surface crack formation or lead gold nanoislands to separate more. As binary images of samples show, this effect is much greater in sample S_{RT} than in sample S_{600}. In the sample S_{RT}, the formation of fine surface cracks after hydrogen exposure is detectable, whereas in the sample S_{450} or S_{600}, hydrogen does not have a significant effect on the Au NPs coupling strength change. Therefore, the plasmonic coupling of Au NPs is responsible for different LSPR wavelength and for the blue shift after hydrogenation. Since the formation of surface cracks is irreversible, the sensor response is also expected to be irreversible. So these types of sensors are practically disposable and colorimetric type, but they can be very accurate in measuring gas (or any other chemical and biochemical agent) concentrations due to their plasmonic mechanism [11].

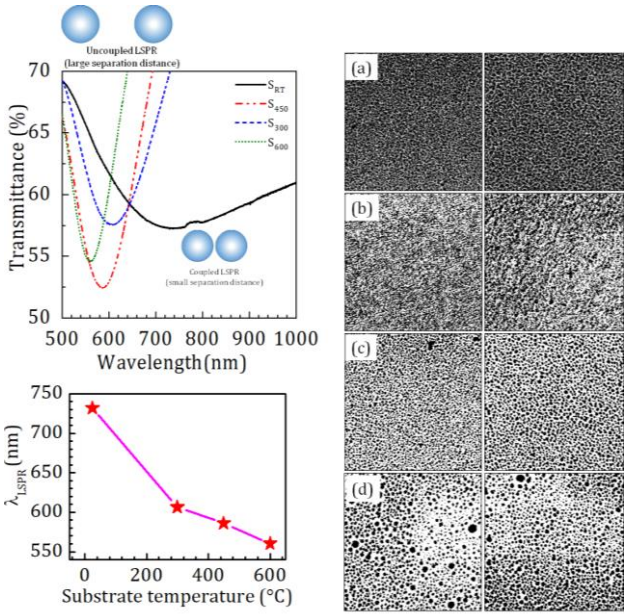


Fig. 1: Left panel top: Optical transmittance spectra of Pd/Au samples deposited at different substrate temperatures. Low panel indicates the LSPR wavelength for different substrate temperatures. Right panel: Binary images taken from the FESEM images for (a) S_{RT}, (b) S_{300}, (c) S_{450} and (d) S_{600}, before and after 10% hydrogen exposure.

3.2. LSPR hydrogen detection

The above data showed that our Pd/Au samples are capable of detecting hydrogen. In the following, we attempt to study their response for different gas concentrations. For hydrogenation, the sample was placed in a UV-Vis spectrophotometer, then, by using a 60 cc syringe filled of hydrogen gas, samples exposed to hydrogen at a specified distance and immediately the spectrum was taken. Hydrogen tests were performed, at room temperature. To investigate the LSPR response of the samples to hydrogen exposure, we measure transmittance spectra for Pd/Au samples with various hydrogen concentration of 0, 0.2, 0.5, 1, 2, 4, 6, 8 and 10% diluted with Ar (shown in Fig.2). The accuracy of the UV-Vis spectrophotometer is 0.1 nm. For error

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reduction, the sample was fixed while exposing to hydrogen gas and measuring the transmittance spectrum. In all the samples, with increasing the hydrogen concentration, gold LSPR wavelength blue shifts to lower wavelengths. The LSPR shifts, shown by arrows inside the spectra for the maximum exposed gas concentration (10%), are 12.6, 7, 3.4 and 0.5 nm for S_{RT}, S_{300}, S_{450} and S_{600}, respectively. Therefore, the layer created at room temperature provides the most spectral shift, among other samples, and is expected to be a better candidate for plasmonic-based hydrogen sensing. The schematic of Pd/Au nanoislands and the spectral shift of gold plasmon peak, before and after exposing to hydrogen gas are shown in fig.3.

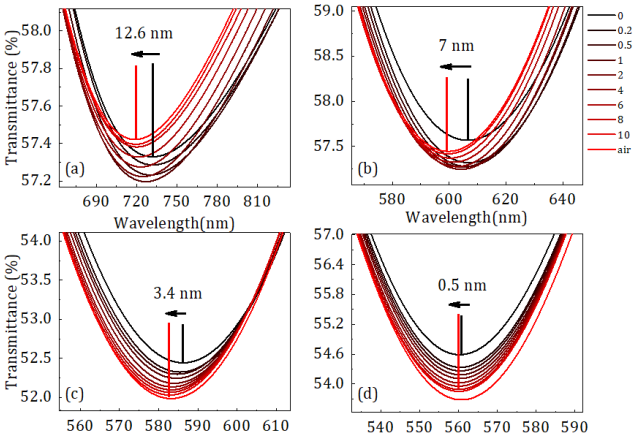


Fig. 2: Transmittance spectra for Pd/Au samples with a hydrogen content of 0, 0.2, 0.5, 1, 2, 4, 6, 8 and 10% for (a) S_{RT}, (b) S_{300}, (c) S_{450} and (d) S_{600} sample.

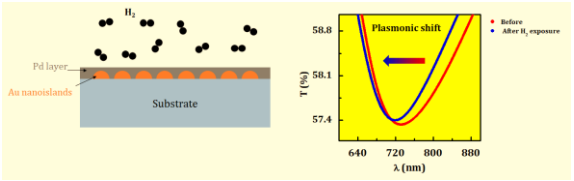


Fig. 3: schematic of Pd/Au nanoislands (left) and the spectral shift of gold plasmon peak, before and after exposing to hydrogen gas (right).

Conclusion

In this paper we show that plasmonic coupling of Au nanoislands can be used for hydrogen sensing. For this purpose, gold nanoislands films were made using PLD method and were examined in the presence of a catalytic layer (Pd). We found that the closer the islands were to each other, the greater the sensitivity to hydrogen based on spectral shift, which we attributed to both NIR and plasmonic coupling. In fact, we attribute the plasmonic coupling intensity change to the palladium layer volume change.

Acknowledgements

The authors would like to thank the Iranian National Science Foundation (INSF) for their financial support.

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