Araştırma Makalesi / *Research Article* **Iğdır Üniversitesi Fen Bilimleri Enstitüsü Dergisi, 9(3): 1377-1384,2019**
Fizik / Physics ***Journal of the Institute of Science and Technology*, 9(3): 1377-1384,2019**

DOI: 10.21597/jist.513363 **ISSN: 2146-0574, eISSN: 2536-4618**

Gold/palladium (Au/Pd) Bimetallic Thin Film Deposition by Radio Frequency Magnetron Sputtering Technique

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ABSTRACT: In this study, two gold/palladium (Au/Pd) thin films having 20 nm and 80 nm thickness values were simultaneously deposited on glass substrates by adjusting target-substrate distance via radio frequency (RF) magnetron sputtering technique. The optical and surface properties of the produced thin films were investigated by using UV-VIS spectrophotometer, interferometer, tensiometer and atomic force microscope. The effects of film thickness on the investigated properties of the thin films were reported.

Keywords: Bimetallic thin films, optical properties, surface properties, low surface free energy

Radyo Frekans Magnetron Sıçratma Tekniği ile Altın/Paladyum (Au/Pd) Bimetalik İnce Film Biriktirme

ÖZET: Bu çalışmada, 20 nm ve 80 nm kalınlığa sahip iki adet altın/paladyum (Au/Pd) ince film, eş zamanlı olarak radyo frekans (RF) magnetron sıçratma tekniği ile hedef-alttaş mesafesinin ayarlanmasıyla cam alttaşlar üzerinde biriktirilmiştir. Üretilen ince filmlerin optik ve yüzey özellikleri UV-VIS spektrofotometre, interferometre, tansiyometre ve atomik kuvvet mikroskobu kullanılarak incelenmiştir. Film kalınlığının, ince filmlerin incelenen özellikleri üzerindeki etkileri rapor edilmektedir.

Anahtar Kelimeler: Bimetalik ince filmler, optik özellikler, yüzey özellikleri, düşük serbest yüzey enerjisi

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Geliş tarihi / *Received:*16.01.2019
Kabul tarihi / *Accepted:*10.04.2019

INTRODUCTION

Preparation of metallic nanoparticles (NPs) with various compositions, structures, shapes and sizes is a matter of interest due to their unique catalytic, electronic, and optical properties (Fedrigo et al., 1993; Kreibig and Vollmer, 1995; Palpant et al., 1998; Bonet et al., 1999). During the past years, more attention is paid to the preparation of bimetallic NPs that are composed of two different metal elements (Szabo and Vollath, 1999; Hodak et al., 2000; Hodak et al., 2000; Maye et al, 2000; Shao et al., 2015; De Yuso et al., 2017). Because, they can exhibit peculiar electronic, optical, and catalytic properties that are absent in the corresponding monometallic NPs (Cybula et al., 2014). Therefore, they are expected to have potential applications in many technologies such as opto-electronic nanodevices, catalysts, and chemical sensors (Kan et al., 2003; Yi et al., 2005; Ferrer et al., 2007). Bimetallic gold/palladium (Au/Pd) NPs can be considered one of the most popular among various alloy nanomaterials (Toshima et al., 1992; Toshima and Yonezawa, 1998; Henglein, 2000; Mizukoshi et al., 2000; Wu et al., 2001; Kan et al., 2003; Li et al., 2004; Zhang and Yin, 2012). Au/Pd, bimetallic solid solution with their atoms located in nanostructures provides synergistic interaction, which leads to enhanced electrical, physical, and chemical properties (Mallikarjuna et al., 2019). Consequently, bimetallic Au/Pd NPs finds wide applications in different fields (Chowdhury et al., 2018). At this point, magnetron sputtering technique is very helpful as an effective way which exhibit properties of great technological importance. In this paper, the synthesis procedure and some physical properties of the Au/Pd bimetallic thin films fabricated by RF magnetron sputtering technique are reported. As far as is known, there is a study on the production of Au/Pd thin films by an another physical deposition technique (Parajuli et al., 2019). However, there is no study in the literature that reports the optical and surface properties of Au/Pd thin films produced by RF magnetron sputtering technique.

MATERIAL AND METHODS

Fabrication of thin films

In the current research, two Au/Pd thin films were simultaneously deposited on glass microscope slides positioned at 30 mm and 45 mm away from the sputter gun by means of RF magnetron sputtering technique. A 99.99% pure Au/Pd target was used as source material. The dimensions of the glass substrates were 75 mm × 25 mm × 1 mm. 99.99% purity argon (Ar) gas was the buffer gas. 13.56 MHz RF power was adjusted to 125 W. Working pressure was approximately 3×10^{-1} Torr. The deposition process was carried out for 60 minutes under these conditions. Deposition parameters are summarized in Table 1.

Table 1. Sputtering parameters of Au/Pd thin films

RF power (W)	Substrate to target distance (mm)	Working pressure (Torr)	Time (min)
125	30 & 45	3×10^{-1}	60

Characterization of thin films

In order to determine the thickness and the refractive index values of the deposited Au/Pd thin films, surface reflections were measured in the wavelength range of 400-1000 nm by a Filmetrics F20 thin film analyzer. The transmittance and absorbance spectra of the thin films were obtained by an UNICO UV-VIS spectrophotometer between the wavelengths 300 nm and 1000 nm. The surface morphologies of the thin films were investigated using an Ambios Q-Scope atomic force microscope (AFM). The surface contact angles of water drop on the thin films and the surface free energies of the thin films were measured by using an Attension Tensiometer.

RESULTS AND DISCUSSION

Reflectometry studies

The obtained reflectance spectra of the produced Au/Pd thin films are presented in Figure 1. The reflectance spectrum of the bare microscope slide is also given in the same figure for better comparison. The film thickness values estimated from the reflectance analysis were approximately 20 nm and 80 nm. It was observed that the target-substrate distance affected the film thickness as expected and the thickness value decreased with the increasing target-substrate distance. The reflectance value increased with the increasing film thickness due to the metallic property of the produced thin films.

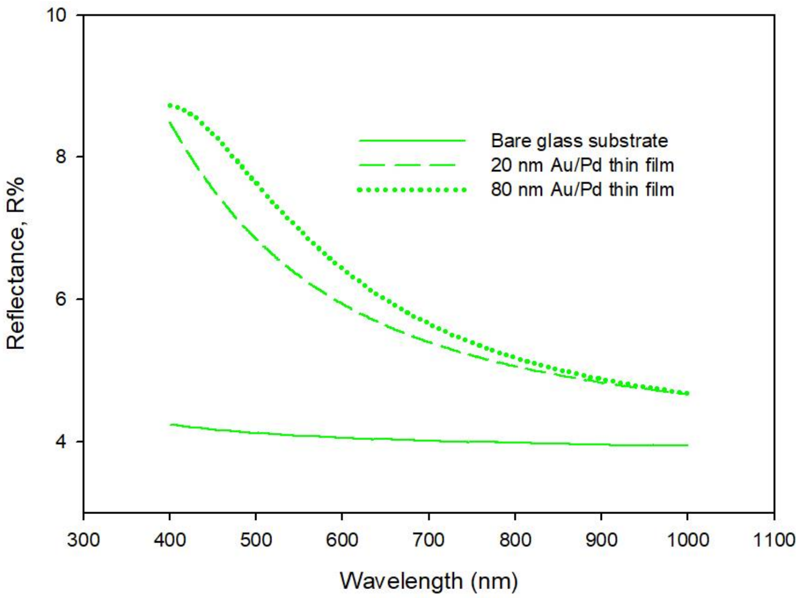

Figure 1. The reflectance spectra of the produced thin films

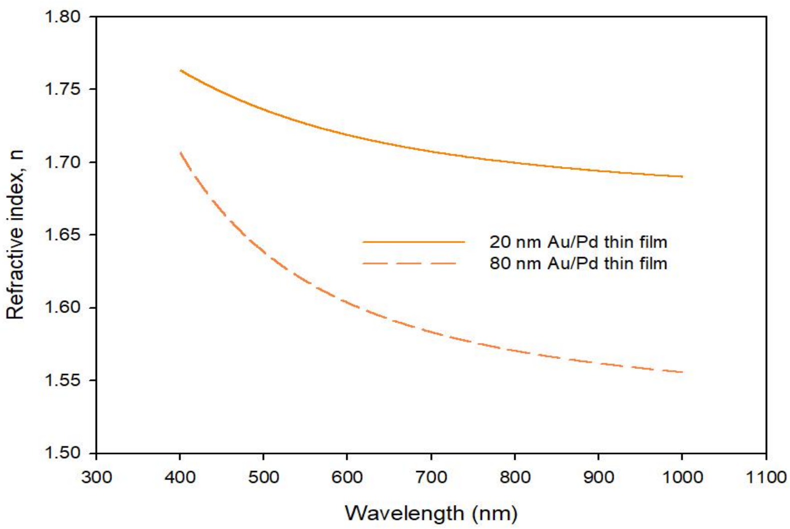

Figure 2. The refractive index distribution of the produced thin films

Refractive index values of the produced Au/Pd thin films versus wavelength are shown in Figure 2. Refractive index measurements were realized using Cauchy model. Cauchy equation for the refractive index is given by:

$$n(\lambda)=A_n+B_n/\lambda^2+C_n/\lambda^4 \text{ and } k(\lambda)=0 \qquad (1)$$

where A_n, B_n and C_n are the fitting parameters used in Cauchy model. Although the refractive index values of both thin films decreased with the increasing wavelength, the refractive index of the thinner film was found to be higher than that of the thicker one. This result is due to the decreased packing density of the film with the increasing film thickness. Refractive index values at the wavelength of 550 nm were determined as 1.72 and 1.61 for 20 nm and 80 nm films, respectively. These values are higher than the refractive index values of the same material in the literature (DeSantis and Skrabalak, 2012).

Ultraviolet and visible spectroscopy studies

The transmittance and absorbance spectra of the bare glass substrate and the produced thin films are presented in Figure 3 and 4. It was observed that the transmittance value noticeably decreased and absorbance increased with the increasing thickness of the Au/Pd thin film due to the thickness effect, because more states are available for the photons to be absorbed in relatively thicker films. The obtained absorbance values are lower than the absorbance values of the same material in the literature (Smith et al., 2016).

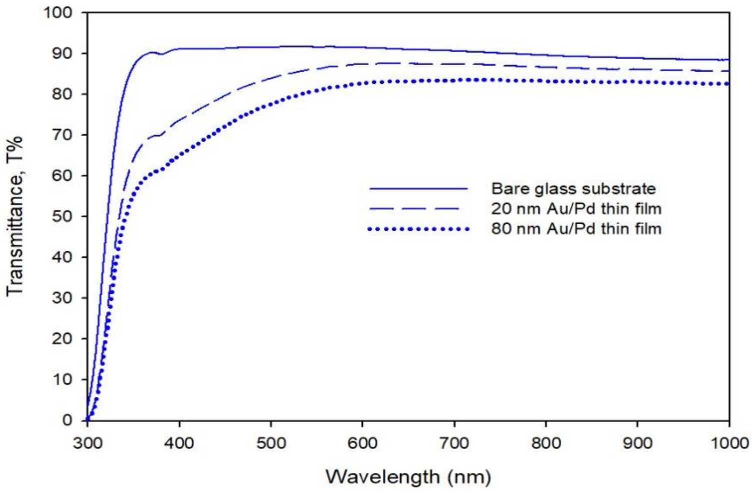

Figure 3. The transmittance spectra of the bare glass substrate and the produced thin films

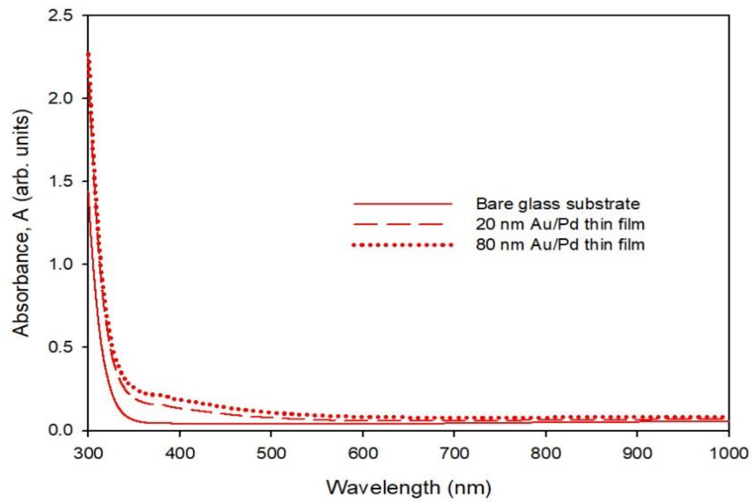

Figure 4. The absorbance spectra of the bare glass substrate and the produced thin films

Atomic force microscopy studies

The obtained two-dimensional (2D) and three-dimensional (3D) AFM images are shown in Figure 5. 3D AFM images reveal that the produced Au/Pd thin films are made up of needle-like grains. Root mean square (RMS) is an important parameter to describe the surface roughness by statistical methods. The mathematical definition and the digital implementation of this parameter are as follows:

$$R_q = \sqrt{\frac{1}{l}\int_0^l \{y(x)\}^2 dx} \quad (2)$$

$$R_q = \sqrt{\frac{1}{n}\sum_{i=1}^{n} {y_i}^2} \quad (3)$$

The RMS mean line is the line that divides the profile so that the sum of the squares of the deviations of the profile height from it is equal to zero. The RMS of the surface roughness of the produced films obtained from 40 lines on imaging scale are 5.31 nm and 8.24 nm for 20 nm and 80 nm films, respectively. These values are higher than the reported RMS values for the surfaces of Au/Pd thin films produced via electron beam thermal evaporation by Nazarpour et al. (Nazarpour et al., 2010). As a result, the surface roughness of the synthesized Au/Pd thin films increases with the increasing film thickness. This observation is in good agreement with relevant literature (Xin et al., 2010).

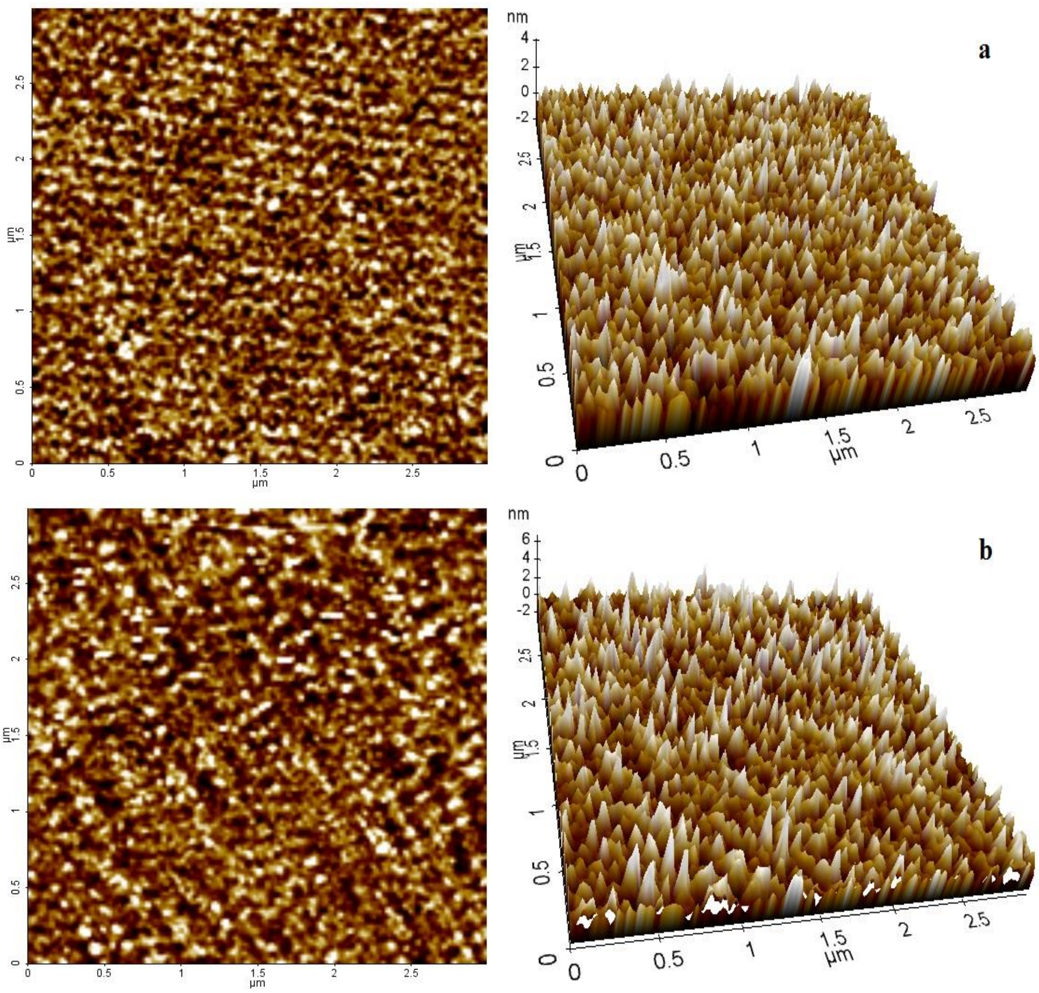

Figure 5. 2D and 3D AFM images of the produced (a) 20 nm and (b) 80 nm thin film

Wettability studies

The interaction between deionized water drop and the surfaces of the produced Au/Pd thin films were analyzed and the contact angles were found to be 77° and 74° for the 20 nm and the 80 nm thin films, respectively. When the water contact angle is smaller than 90°, the solid surface is considered hydrophilic. The photo images of the water drop on the film's surfaces are presented in Figure 6. The surface free energy (SFE) values of the thin films were measured as 35 mJ/m^2 for the 20 nm film and 37 mJ/m^2 for the 80 nm film. These values are lower than the SFE values of other materials in the literature (Jerman et al., 2010; Shin et al., 2012). The observation is that the surface morphology of the produced thin films affects the contact angle values. On needle-like surfaces, the contact angle value increases and the surface free energy value decreases.

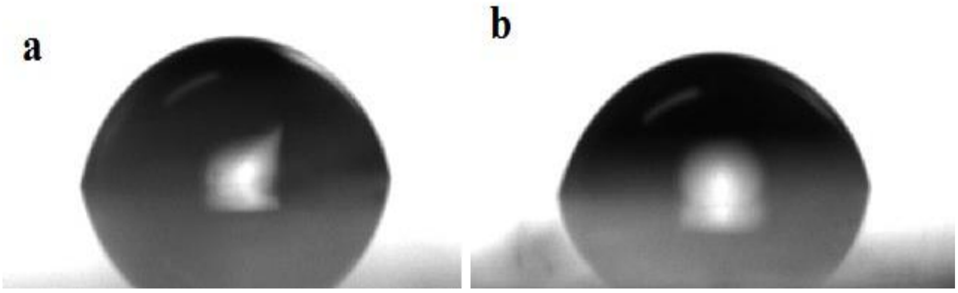

Figure 6. Photo images of water drop on the produced (a) 20 nm and (b) 80 nm thin film

CONCLUSION

In conclusion, two Au/Pd thin films having different thickness values were deposited on glass substrates by means of RF magnetron sputtering technique. From the findings of the optical investigations, the films have high transmittance and low absorbance in the visible region as they are very thin layers. It was also observed that the reflectance and absorbance increase while transmittance and refractive index decreases with the increasing film thickness. The results of AFM studies show that the surfaces of the films are smooth (having low RMS roughness values) and homogenous with needle-like grains. However, roughness increases with increasing thickness. The surfaces of the produced Au/Pd thin films have low SFE values and they show hydrophilic properties in wetting experiments.

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