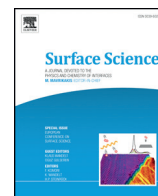




Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Surface structure characterization of ultra-thin films of Au deposited on Pd(111)

A. Pancotti^a, A. de Siervo^b, P.A.P. Nascente^{c,*}, R. Landers^b

^a Regional Jataí, Departamento de Física, Universidade Federal de Goiás, CEP 75801-615, Jataí, GO, Brazil

^b Departamento de Física Aplicada, Instituto de Física "Gleb Wataghin," Universidade Estadual de Campinas, CEP 13083-859, Campinas, SP, Brazil

^c Departamento de Engenharia de Materiais, Universidade Federal de São Carlos, CEP 13565-905, São Carlos, SP, Brazil

ARTICLE INFO

Available online xxxx

Keywords:

Gold-palladium alloys
Bimetallic surfaces
X-ray photoelectron diffraction
Synchrotron radiation
Low-energy electron diffraction
Surface alloys

ABSTRACT

Ultra-thin films of Au were deposited on the Pd(111) surface and then characterized by X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), and X-ray photoelectron diffraction (XPD) generated by synchrotron radiation. The Au films were deposited at room temperature (300 K) and subsequently annealed at 400 °C (673 K) and 610 °C (883 K). XPD analyses indicated that the gold films were 7 and 6 ML thick, for the annealing temperatures of 400 °C and 610 °C, respectively. The film interlayer distances exhibited an oscillatory behavior, with a 5% contraction between the top and the second layers, a 3% expansion between the second and the third layers, for the film annealed at 400 °C, and a 2% expansion in the interlayer distance between the top and the second layers and a 4% contraction between the second and the third layers, for the film annealed at 610 °C. For both annealing temperatures, the interlayer distances between the third and the fourth layers and between the fourth and the fifth layers exhibited a 1% expansion and a 2% contraction. For the film annealed at 610 °C, XPD results revealed that the Pd(111) surface was covered by Au islands, with some bare patches exposed.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Bimetallic surfaces have attracted considerable interest due to their interesting catalytic, electronic, electrochemical, and magnetic properties [1–5]. The deposition of an ultra-thin metal film on a single-crystal metal substrate can produce a bimetallic surface. The ultra-thin films constituted by transition and noble metals present particular interest in heterogeneous catalysis since bimetallic surfaces have shown an enhanced activity for catalytic reaction as compared to pure metals [1–3,6].

While palladium is an excellent catalyst for many reactions, gold alone is considered as a poor catalyst; however, the activity and selectivity of Pd catalysts can be significantly enhanced by the addition of Au [7,8]. Au and Pd are completely miscible in all proportions and there is only a slight lattice mismatch (less than 5%) between Au(111) and Pd(111) [9]. Thus, pseudomorphic overlayers of Pd on Au(111) and Au on Pd(111) can be prepared [10–12]. No ordered LEED structures other than the substrate (1×1) pattern have been observed for Au overlayers deposited on Pd(111), and the lattice spacing was found to vary linearly with alloy composition, implying the formation of surface alloys [10–13].

Wessman-Wenocur et al. [10] used Auger electron spectroscopy (AES), LEED, and photoemission spectroscopy (PES) generated by

synchrotron radiation to investigate the composition, surface structure, and electronic structure of Au overlayers on Pd(111) ranging from 0.1 to 10 monolayers (ML). LEED patterns showed the formation of an ordered Au(111) overlayer on the Pd(111) substrate. The following effects were observed by PES: (1) structures appeared which merged smoothly into the Au structure, (2) structures at the energies of the bare Pd substrate peaks were sharpened when submonolayers of Au were deposited, and (3) a new structure appeared was presumably due to Pd–Au hybridization upon alloying.

Kuk et al. [11] studied the epitaxial growth of Au on Pd(111) by ion scattering spectroscopy (ISS), AES, and LEED. They observed a sharp transition from a pseudomorphic growth to a state with misfit dislocations and strain for a critical thickness of approximately 2 Å.

Baddeley et al. [12] employed AES and LEED to characterize the surface of an ultra-thin film (approximately 4 ML) of Au deposited on Pd(111) at room temperature (300 K). They reported that annealing of Au overlayers on Pd(111) caused the formation of random Au–Pd surface alloys with increasing Pd content. No ordered superstructure was observed in the temperature range of 300 to 1200 K other than the substrate (1×1) pattern.

Gleich et al. [14] studied the CO adsorption on the surface of Au/Pd(111) by AES, LEED, high-resolution electron energy loss spectroscopy (HREELS), and scanning tunneling microscopy (STM). For the deposition of 0.26 ML Au on Pd(111) at 100 K, the substrate was covered by a large number of small Au islands (average island size of about 20 Å). The deposition of 0.2 ML Au at 300 K also yielded the formation of larger Au islands (average diameter of about 300 Å). The deposition of 1.3 ML Au at 300 K

* Corresponding author at: Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, CEP 13565-905, São Carlos, SP, Brazil.
E-mail address: nascente@ufscar.br (P.A.P. Nascente).

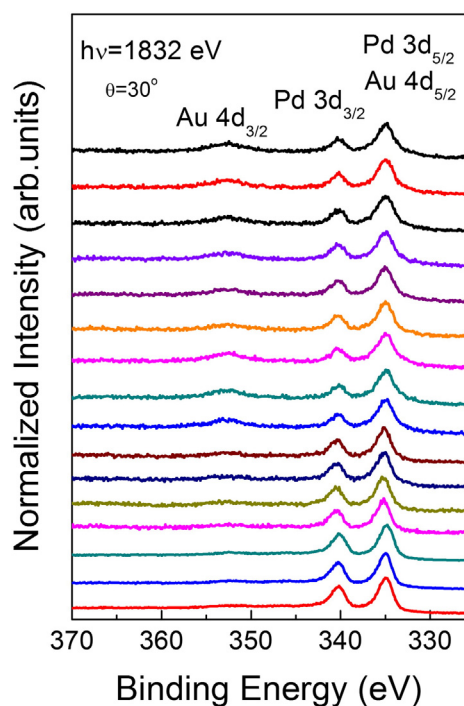


Fig. 1. Au 4d and Pd 3d XP-spectra obtained during the Au film growth on Pd(111) at room temperature.

and subsequent annealing up to 925 K caused the diffusion of Au into the Pd(111) bulk. After this annealing process, the surface did not exhibit islands on the flat terraces nor extra structures at the step edges.

Tysoe et al. examined the surface alloy formation for Au deposited on Pd(111) by AES [13], XPS [13], CO chemisorption [13], LEED [15], low-energy ion scattering (LEIS) [15], Monte Carlo [16], and density functional theory (DFT) [16] analyses. They reported that Au film grew in a layer-by-layer mode at 300 K, and Au started to diffuse into the Pd bulk after annealing to above approximately 600 K. CO desorption activation energies and vibrational frequencies were consistent with preferential segregation of Au to the surface [13]. For the deposition of 5 ML Au at 300 K, LEED and LEIS also indicated a significant enrichment of Au at the surface [15]. The same group also reported on the adsorption and reaction of ethylene [17], acetic acid [18], and vinyl acetate [19–21] on Au/Pd(111) alloy surfaces. The formation of Au–Pd alloys had a considerable effect on the surface chemistry of the adsorbed molecules.

A more complete experimental and theoretical investigation of the Au–Pd system is justified due to its importance. This work is an extension of our previous study on the reverse system: ultra-thin films (1 and 3 ML) of Pd deposited on Au(111) [22]. XPS, X-ray excited Auger spectroscopy (XAES), LEED, and X-ray photoelectron diffraction (XPD) generated by synchrotron radiation were employed in order to characterize the growth, composition, and structure of the two Pd films. For the 1 ML Pd annealed at 450 °C (723 K), XPS and XAES results indicated that Pd had diffused into the Au bulk [22]. For the 3 ML Pd deposited at room temperature (300 K), the comparison between experimental and theoretical XPD results indicated approximately 30% of the surface was formed by 2 ML Au layers, and 70% of the surface, by 1 ML Au layer [22]. In the present study, we have investigated by XPS, LEED, and XPD the surface composition and structure of an ultra-thin Au film deposited on Pd(111) at room temperature (300 K) and subsequently annealed at two temperatures: 400 °C (673 K) and 610 °C (883 K).

2. Experimental and theoretical methods

A 10 mm diameter Pd(111) crystal was mounted on a 1 mm thick Mo plate that could be aligned by laser. The experiments were

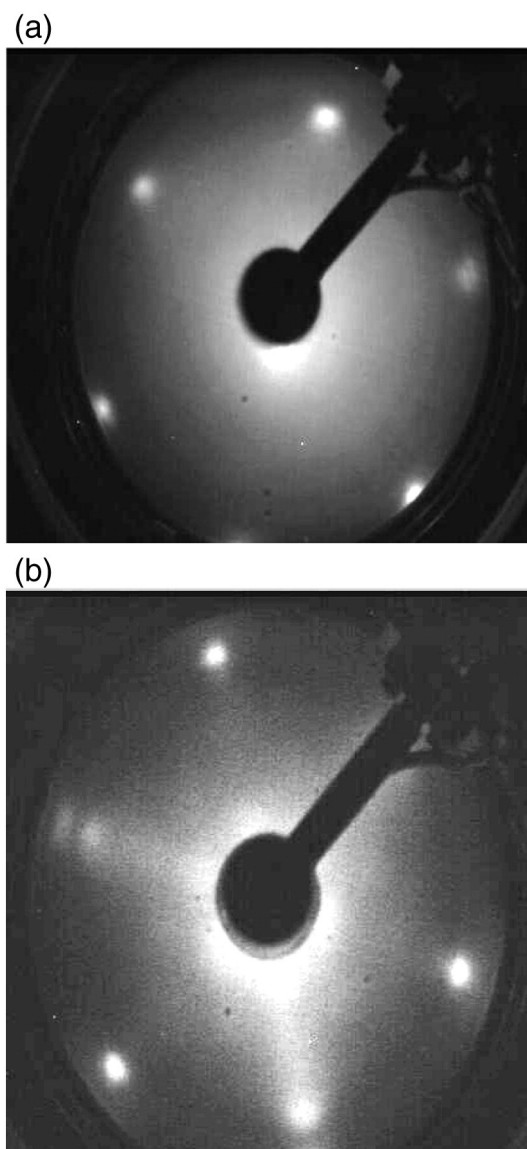


Fig. 2. LEED patterns for 88 eV primary electron energy: (a) clean Pd(111) substrate and (b) Au deposited on Pd(111).

performed at the Brazilian Synchrotron Light Laboratory (LNLS) using the soft X-ray spectroscopy (SXS) beam line, and the measurements were done with a surface analysis system equipped with LEED optics, a high-resolution electron analyzer (Omicron HA125HR with multi-channel-detection) mounted in the plane of the storage ring, a differentially pumped argon ion sputter gun, a two axis sample manipulator, and a conventional Al K α (1486.6 eV) X-ray source [22]. The base pressure was always less than 2×10^{-10} Torr during the analyses. It was used an InSb(111) monochromator and the synchrotron photon energy was 1832 eV.

The Pd(111) crystal was cleaned in UHV by cycles of argon ion sputtering (900 V accelerating potential) for 10 min and annealed using an electron beam (20 mA, 1.0 kV), impinging on the backside of the crystal to heat the sample at about 900 °C (1173 K) for 3 min. The surface was considered to be clean when typical contaminants such as C, O, N, and S were not detected by XPS. The LEED pattern displayed a well-defined (1 \times 1) pattern for the Pd(111) single-crystal substrate surface.

Pieces of gold wire inserted on a Mo crucible heated by electron bombardment were the source for depositing the Au films onto the Pd(111) substrate at room temperature with subsequent annealing at

Download English Version:

<https://daneshyari.com/en/article/5421655>

Download Persian Version:

<https://daneshyari.com/article/5421655>

[Daneshyari.com](https://daneshyari.com)