Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Electron Spectroscopy and Related Phenomena 148 (2005) 80–90

JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena

www.elsevier.com/locate/elspec

Alloying of Pd thin films with Nb(0 0 1)

E. Hüger[a,b], H. Wormeester[c], K. Osuch[d,e]*

[a] Institute of Physics and Physical Technology, Technical University Clausthal, D-38678 Clausthal-Zellerfeld, Germany
[b] Department of Biomaterials, IBA e.V. Rosenhof, D-37308 Heilbad Heiligenstadt, Germany
[c] MESA+ Research Institute, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands
[d] Department of Physics, University of South Africa, P.O. Box 392, Pretoria 0003, South Africa
[e] Institute of Mathematics and Physics, University of Podlasie, 3-go Maja 54, 08-110 Siedlce, Poland

Received 15 June 2004; received in revised form 22 March 2005; accepted 24 March 2005
Available online 10 May 2005

Abstract

Annealing at elevated temperatures (1000–1600 K) of at least 10 ML thick Pd films deposited on Nb(0 0 1) has been found to result in a substrate capped by a pseudomorphic monolayer of Pd. This 1 ML thick Pd cap layer was characterised with a combination of UPS and DFT-calculations. UPS, RHEED and AES show that this cap layer protects the Nb(0 0 1) surface against (oxygen) contamination, which is a well known problem of Nb substrates. AES sputter profiling indicates that a major part of the Pd material in excess of the pseudomorphic monolayer is dissolved in the Nb lattice just below the surface. XPD shows that these dissolved Pd atoms occupy substitutional sites in the substrate. The analysis of the XPS-anisotropy also provides some information about the concentration and positions of the Pd and Nb atoms in the alloyed samples.

PACS: 68.43.-h; 82.80.Pv; 73.20.At; 82.45.Jn; 75.50.Cc; 71.15.Mb

Keywords: Niobium; Palladium; Photoelectron spectroscopy (PES); Surface composition; Electron diffraction

1. Introduction

The bimetallic bonding in binary alloys can lead to new and unique chemical properties of metals. This is a result of significant differences in the band structure of an alloy compared to the band structure of the constituting metals[1]. The largest metal–metal interaction occurs when a binary mixture is made up of an almost fully occupied valence band metal (like Ni and Pd) and an almost empty valence band metal (like Nb and Ta). For novel chemical reactivity properties it is not volume intermixing that is of interest, but rather intermixing in the near surface region and especially at the very surface itself. Many studies of metal–metal bonding have thus focused on Pd deposited on Nb(1 1 0) [1–10] and Ta(1 1 0) [1,10–20]. The adsorption of Pd on Nb or Ta was reported to lead to a reactivity similar to that of Ag [1,15–20]. This dramatic change in chemistry with respect to that observed for the mere Nb and Ta substrate was attributed to a pseudomorphic (ps) monolayer (ML) of Pd adsorbed on Nb(1 1 0) and Ta(1 1 0). However, Nb or Ta substrates fully covered by 1 ps ML of Pd are not easy to obtain because: (i) a phase transition from a commensurate ps Pd structure to an incommensurate Pd(1 1 1) film is observed within the first ML if Pd is deposited by vapour deposition on Nb(1 1 0) or Ta(1 1 0) at or below room temperature[3,12,16] and (ii) the preparation of contamination free Nb and Ta surfaces is not straightforward and contamination hampers the preparation of a substrate capped by a ps ML of Pd. For instance, oxygen contamination is known to negatively change the film growth mechanism and influence the structure of a film[14,15]. (iii) The calibration of exactly 1 ps ML deposited on a substrate is difficult.

A more convenient method of preparing inert, stable, easily reproducible, contamination free Nb or Ta surfaces covered by a ps ML of Pd is to deposit a large quantity of Pd on the substrate surface and subsequently anneal the sample at elevated temperatures [9–13,15,16]. This idea is based on the fact that at high temperatures (1000–1300 K) Pd atoms in excess of 1 ML leave the surface, either through desorption or through diffusion into the substrate. The annealing

---

* Corresponding author. Tel.: +27 12 4298666; fax: +27 12 4293643.
E-mail address: osuchk@science.unisa.ac.za (K. Osuch).

0368-2048/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.elspec.2005.03.003

thus leads to Nb(1 1 0) or Ta(1 1 0) substrates covered with 1 ps ML of Pd [9]. Low energy electron diffraction (LEED) indeed shows that this procedure leads to as sharp spots as those obtained from the clean substrate surface [9]. This indicates far better long-range order than that observed for an 'as-deposited' ps Pd. Ultraviolet photoelectron spectroscopy (UPS) measurements show a large similarity between the surfaces obtained with these two methods. The annealing only increases the intensity of the emission features and sharpens them in comparison to those of the 'as-deposited' ps Pd films [10]. Sagurton et al.[9] calibrated the deposition rate of Pd on Nb(1 1 0) through attributing the UPS spectra of an annealed Pd sample to a ps ML of Pd and compared this to the set of UPS spectra collected during the deposition of Pd. Auger electron spectroscopy (AES) measurements of the ps Pd films obtained after annealing showed a higher Pd AES signal than that of the 'as-deposited' ML of Pd [12,15,16]. Koel et al.[16] assigned this to Pd crystallites situated on-top of the ps ML. A comparison of temperature programmed desorption (TPD) data from Pd deposited on Ta(1 1 0) with Pd deposited on W(1 1 0) leads to the conclusion that there also occurs diffusion of Pd into the bulk of Ta. [15,16]. Ruckmann et al. [12] found that the Pd Auger and X-ray photo-electron spectroscopy (XPS) lines show a larger core-level shift for the high temperature annealed substrate. This means that more Pd material with predominantly (nearest neighbour) Pd–Nb bonds must remain after annealing, than in the 'as-deposited' 1 ML Pd sample.

In this paper, we investigate the anneal behaviour of thin Pd films deposited on Nb(0 0 1). X-ray photo-electron diffraction (XPD) and AES sputter-profiling show unambiguously that the annealing procedure leads to the formation of a Pd–Nb alloy just below the surface. Experimental results are further obtained from XPS, reflection high-energy electron diffraction (RHEED) and UPS. The latter measurements are supported by self-consistent density functional theory (DFT) calculations. We show on the grounds of experimental data that the anneal between 1000 and 1500 K of thin Pd films deposited on Nb(0 0 1) leads to: (i) a Nb(0 0 1) surface fully covered by a ps ML of Pd; (ii) the dissolution in a substitutional way of a significant part of the Pd film in excess of the ps ML in the near surface region of the Nb bulk. We first describe the experimental and theoretical methods employed. The presentation and discussion of the data starts by showing that, despite the similar growth of Pd on Nb(0 0 1) and W(0 0 1), the anneal behaviour for Pd deposited on Nb(0 0 1) is very different from that of Pd on W(0 0 1).

2. Experimental setup and electronic structure calculation procedure

2.1. Measurement equipment

The experiments were performed in a VG-ESCA-LAB MKII spectrometer, to which a home-built chamber equipped with a RHEED apparatus was attached. The RHEED chamber was pumped by a titanium sublimation pump with a wall cooled with liquid nitrogen (LN_2) and via the main system by a LN_2-baffled diffusion pump which produces a base pressure of 3×10^{-11} mbar. During the metal deposition from pre-outgassed evaporators situated in both chambers the pressure rose to 7×10^{-11} mbar. The home-built water-cooled metal evaporators allowed deposition rates of 0.03–10 monolayers (ML) per minute.

The surface quality and growth mode were examined with RHEED, AES and angle resolved ultraviolet photoelectron spectroscopy (ARUPS). The geometric structure was determined with RHEED and XPD, the electronic structure with ARUPS. The chemical composition of the sample was checked mainly with AES. A VG-Microtech EX05 ion source was used for sputtering. The ion sputtering was always performed at room temperature. Sputter profiling was done through simultaneous ion sputtering and AES or UPS measurements.

For RHEED measurements, a 20 keV electron beam (emission current 9 μA) at grazing angles of incidence ~0.3° was used. A Faraday cup detector was used to measure the intensity oscillations of the specular reflected electron beam. The Faraday cup could be moved into any desired position in the central part of the RHEED pattern which was simultaneously observed on a fluorescent screen.

The main chamber (ESCA) contained an hemispherical analyser with the resolution of 60 meV at the pass energy of 2 eV, a monochromatised Al Kα X-ray source and an electron gun for AES, operated at the emission current of 1–3 μA, the beam energy of 1.8 keV, and the beam diameter of 0.2–1 mm at the sample. The Auger signal was differentiated by modulation of the target potential with 3 V (peak-to-peak) for the detection of impurities and with 1 V (peak-to-peak) for in situ monitoring of the film growth. For (AR)UPS measurements a Leybold capillary noble-gas resonance discharge lamp with the photon energy of 21.22 eV (HeI) was used. A polariser made it possible to use both polarised and unpolarised light. For AES and XPS the angular acceptance of the analyser was set to ±12°, for XPD and ARUPS to ±1°.

2.2. Electronic structure calculation

The calculations were performed within the framework of DFT, using the full potential linearised plane wave (FLAPW) method and the local spin density approximation (LSDA) [23,24] as implemented in the Wien2k package [25]. First scalar relativistic calculations were carried out and subsequently spin-orbit coupling was included in a second variation step [25]. A 132 k-points were used in the appropriate irreducible wedge of the Brillouin zone. The adsorption systems were simulated with a slab model, which is known to be very efficient and precise for various surface problems[26]. The unit cell of the slab was for all adsorption systems a tetragon with the height equal to 18 non-relaxed Nb(0 0 1) MLs (18×1.65 Å), and whose base was equal to the two-