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RHEED study of the growth of Pd–Al/MgO bimetallic system

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Abstract

A Pd–Al bimetallic system was prepared on a MgO (0 0 1) single-crystalline substrate surface by vacuum deposition. The early stages of the growth in dependence of Pd and/or Al deposition sequence were studied. The reflection high-energy electron diffraction method was used for structural investigation during the deposition. The results can be interpreted in terms of formation of stable Pd–Al alloy covered by an aluminum overlayer. Under all deposition conditions the diffraction patterns indicated that the Pd–Al system is composed of three-dimensional epitaxial particles having the following orientation relationship with respect to the substrate surface: Pd–Al (0 0 1) || MgO (0 0 1), Pd–Al [1 1 0] || MgO [1 1 0]. When Pd was deposited at first the evolution of lattice parameter and diffraction spot intesity during the growth showed the formation of a Pd pseudomorphic layer which was spread by a strong Pd–Al bimetallic interaction during subsequent Al deposition. Applying the opposite sequence of deposited materials or simultaneous deposition of both metals three-dimensional growth of clusters was observed from the beginning of the deposition process.

Keywords: Palladium; Aluminum; Clusters; Reflection high-energy electron diffraction (RHEED); Electron energy loss spectroscopy (EELS); Pd–Al thin films

1. Introduction

In the recent years, great effort has been made to investigate the structural, electronic and chemical properties of bimetallic systems. It is well known that a bimetallic surface can exhibit chemical and catalytic properties that are very different from those of the individual metals. Large effects were observed for bimetallic surfaces that combine a metal with an electron-rich d band (late transition metal) and a metal with an electron-pure valence band (early-transition or sp metal). Bimetallic bonding can induce significant changes in the band structure of a metal, opening in this way the possibility for preparation systems exhibiting new and unique chemical properties [1]. Due to a very strong Al–Pd interaction [2–4] new

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bimetallic catalysts based on the Pd/Al alloy can be developed [5,6].

The X-ray photoelectron spectroscopy (XPS) investigation of Pd/Al alloy indicated a strong bimetallic interaction resulting in a noble metal-like electronic structure. The structural studies performed by the reflection high-energy electron diffraction (RHEED) method showed that it was possible to prepare heteroepitaxial Pd/Al clusters having fcc Pd-like crystal structure on KCl (0 0 1) [7]. The physical and chemical properties of bimetallic systems are given by bimetallic interaction as well as by their structure and morphology. To study these influences the model systems epitaxial layers deposited on single-crystalline substrates can be used.

In this work, the early stages of the growth of a Pd–Al bimetallic system in dependence of Pd and/or Al deposition sequence were studied. The RHEED method was used for structural investigation during the deposition. The results of this study represent evolution of structural parameters of the Pd–Al bimetallic system during its growth under three different deposition conditions: (i) Pd deposition followed by Al deposition, (ii) Al deposition followed by Pd deposition and (iii) simultaneous Pd and Al deposition.

The above-mentioned results were completed by reflection high-energy electron loss spectroscopy (RHEELS) measurements. The energy losses are characteristic for the surface structure and chemical composition of the sample [8,9]. The combination of RHEED and RHEELS methods is especially useful in early stages of thin film growth when the intensity of a diffraction pattern is too low.

2. Experimental details

The studies were performed in a specially designed UHV system equipped with a RHEED facility permitting simultaneous observation of the substrate surface during deposition. The instrument was operated at an acceleration voltage of 25 kV. The diffraction pattern was recorded by an RHEED—vision computer system consisting of CCD camera, video recorder and a computer. Special software equipment permitted to obtain the position of diffraction spots with a very high precision [10] and by this way to evaluate the lattice parameters of the deposit. Apparatus was equipped with retarding field like energy analyser RHEA-100 (STAIB INSTRUMENTS). A retarding field isolates those diffracted electrons, which interact with the investigated surface and experience appropriate energetic loss. A lock-in technique is than used to provide the EELS spectrum.

Pd was deposited using a special evaporation cell (MEBES, Micro Electron Beam Evaporation Source) [11] operating at a very low evaporation rate of 0.1 monolayer (ML) per minute, approximately. Al was deposited from a Knudsen cell-like source using an alumina crucible. The evaporation rate was estimated to be more than three-times higher than for Pd. Although the background pressure in the vacuum chamber was better than 1×10^{-7} Pa the deposition was carried out at a pressure about 1×10^{-6} Pa due to the high thermal load of evaporation sources. The substrate temperature was maintained at 200 °C during Pd and/or Al deposition.

3. Results and discussion

The (0 0 1) MgO single-crystalline substrate was cleaved in air and then immediately introduced into the vacuum chamber. Before the metal deposition the sample was heated at the temperature of 300 °C for 30 min. Fig. 1 represents RHEED diffraction patterns obtained at different steps of experiment in the [1 1 0] crystallographic direction parallel to the primary electron beam. The diffraction pattern taken from clean MgO substrate (NaCl-like structure having lattice parameter $a = 0.42112$ nm) is shown in Fig. 1a. The typical two-dimensional diffraction features can be observed. The pattern consists of lines perpendicular to the substrate surface, which indicate a smooth surface containing large terraces or monoatomic steps.

Fig. 1b shows the RHEED diffraction pattern after the deposition of 1.4 ML, approximately. There is no explicit change in the diffraction pattern. The presence of Pd on the substrate