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Formation of palladium hydrides in low temperature Ar/H_2-plasma

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ABSTRACT

20 nm thick Pd coatings deposited on Si substrates with 800 nm SiO_2 and 1 nm Cr buffer layers were treated in a 2.45 GHz microwave plasma source at 700 W plasma power and 40 Pa working pressure without substrate heating. For obtaining information on the effect of energy influx due to ion energy on the palladium films the substrate potential was varied from $U_{sub} = 0$ V to -150 V at constant gas flow corresponding to mean ion energies E_i from 0.22 $eV \cdot cm^{-2} \cdot s^{-1}$ to 1.28 $eV \cdot cm^{-2} \cdot s^{-1}$.

In contrast to high pressure reactions with metallic Pd, under plasma exposure we do not observe solid solutions over a wide range of hydrogen concentration. The hydrogen incorporation in Pd films takes place discontinuously. At 0 V substrate voltage palladium hydride is formed in two steps to $PdH_{0.14}$ and $PdH_{0.57}$. At -50 V substrate voltage $PdH_{0.57}$ is formed directly. However, substrate voltages of -100 V and -150 V cause shrinking of the unit cell. We postulate the formation of two fcc vacancy palladium hydride clusters $PdH_{Vac}(I)$ and $PdH_{Vac}(II)$. Under longtime plasma exposure the fcc $PdH_{Vac}(II)$ phase forms cubic $PdH_{1.33}$.

The fcc $PdH_{0.57}$ phase decomposes at temperatures > 300 °C to form metallic fcc Pd. The hydrogen removal causes a decrease of lattice defects. In situ high temperature diffractometry measurements also confirm the existence of $PdH_{Vac}(II)$ as a palladium hydride phase. Stoichiometric relationship between cubic $PdH_{1.33}$ and fcc $PdH_{Vac}(II)$ becomes evident from XR measurements and structure considerations. We assume both phases have the chemical composition Pd_3H_4. Up to 700 °C we observe phase transformation between both the fcc $PdH_{Vac}(II)$ and cubic $PdH_{1.33}$ phases. These phase transformations could be explained analog to a Bain distortion by displacive solid state structural changes.

1. Introduction

The behavior of hydrogen in metals has attracted scientific attention for many decades and is interesting from both basic research and technological points of view. Many hydrides find a wide range of applications of which the most prominent is the reversible hydrogen storage. Moreover the high diffusivity of hydrogen also makes nanoscaled metal hydride (MeH) systems interesting possibilities for sensor applications, and surface reactions with hydrogen on Pt, Pd, Ni, and other metals are applied in catalysis, particularly in fuel cells.

Most binary metal hydrides are synthesized by solid gas reactions between metal and hydrogen. The palladium hydrogen system is known for quite some time [1,2,3]. Palladium hydride is metallic palladium that contains a substantial quantity of hydrogen within its fcc crystal lattice. Palladium hydrides may contain two crystalline phases, α and β. The low concentration α-phase with an atomic ratio $H/Pd < 0.1$ and the high concentration β-phase with $H/Pd > 0.6$ were observed at room temperature [4]. These palladium hydrides reveal a defect rock salt structure type and are described as the prototype for interstitial hydrides. Higher hydrogenated phases can be produced in the Pd hydride system by ion implantation or high pressure hydrogenation. Ion implantation of deuterium into Pd was reported to produce concentration as high as 1.3 to 1.6 deuterium atoms per metal atom [5,6]. Fukai et al. [7,8] observed in Pd metal a lattice contraction at high hydrogen pressure (3.5 GPa) and high temperatures (800–900 °C). According to the authors the findings suggest the formation of a lot metal vacancy clusters, so called superabundant vacancies (SAV) [9]. Tavares et al. [10] describe a plasma based ion implantation applied to the Pd–H system. In this experimental study, the Pd samples have been implanted with pulsed high energetic hydrogen ions of 40 keV, corresponding to a pulse voltage of -40 kV. Strong hints suggest formation of a vacancy ordered structure and show thereby that very high pressure hydrogenation is not mandatory to superabundant vacancy phase generation.

A specific challenge in plasma sciences is the investigation of structural changes and chemical reactions in solid surfaces and surface layers when external plasma parameters are varied. The investigation of plasma-surface interaction plays an essential role in low-temperature, low-pressure plasma processing. Compared to the well-known thermally stimulated solid–gas chemistry, little is known about solid–

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plasma chemistry. The effect of low energy plasma species onto solid surface layers is one focus of plasma research. In analogy to experiments with thin metallic nickel films in Ar–H_2 plasma [11,12,13] we have studied the behavior of Pd layers in microwave plasma. The influence of plasma composition and energy fluxes on Pd surface will be studied to understand the synthesis, the chemical composition and formation of crystal structures.

2. Experimental

Thin pure Pd coatings (20 nm) were deposited on Si substrates with 800 nm SiO_2 and 1 nm Cr buffer layers. These films were treated in a microwave plasma source SLAN [14] with 10 sccm Ar/10 sccm H_2 gas mixture without substrate heating. Plasma power and gas pressure were kept constant at 700 W and 40 Pa, respectively. It is difficult to directly modify the behavior of the neutral particles, but charged particles can be controlled by changing the local electric field, and this is the basis of substrate voltage method. Negative substrate voltage accelerates positive ions (Ar^+, Ar_2^+, Ar^{2+}, H^+, H_2^+, ArH^+) towards the Pd film. The substrate voltage was varied in steps of 50 V from 0 V to −150 V. From Langmuir probe diagnostics we calculate increasing mean ion energies from E_i from 0.22 eV·cm^{-2}·s^{-1} at 0 V to 1.28 eV·cm^{-2}·s^{-}1 at −100 V substrate voltages. Within 15 min the energy influx by the Ar/H_2 plasma implements a substrate temperature of about 200 °C. The influence of the used substrate voltage on the substrate temperature is marginal.

The samples were characterized before and after plasma exposure (each with 15 min) by GIXD (grazing incidence X-ray diffractometry, asymmetric Bragg case, incidence angle $\omega = 0.5°$) regarding position, intensities and line profile of observed Bragg reflections and XR (X-ray reflectometry) regarding thickness, density and roughness. Both, GIXD and XR were performed at HASYLAB beamline D4 (E = 10 keV) at DESY and on a Siemens D 5000 diffractometer equipped with a special sample stage for reflectometry measurements and a special parallel beam attachment (parallel beam collimator) for diffractometry investigations. Cu K_α radiation (40 kV, 40 mA) was used.

Hydrogen desorption experiments were done in situ by measuring the X-ray pattern (or single reflections) at elevated temperatures using a Buehler HDK2.4 mounted on a θ–θ diffractometer XRD 3000 (Fa. Seifert). The pressure within the chamber was 0.5 Pa. For each measurement the sample was heated up to a certain temperature with a heating rate of 10 K/min. Measurements were carried out in steps of 100 K.

3. Results and discussion

The formation of palladium hydrides in an Ar/H_2 gas atmosphere depends on plasma impact. X-ray patterns of as-deposited films and films after Ar/H_2 gas treatment under vacuum conditions (40 Pa) do not show any differences. After plasma exposure we observe peak shifts. The formation of Pd hydrides depends on the used substrate voltage and the plasma exposition time. Fig. 1 shows an overview of X-ray patterns of fcc Pd after short time plasma exposure (30 min). The substrate potential U_{sub} was varied from 0 V to −150 V in steps of −50 V. Longtime plasma exposure gives a more detailed insight in the plasma processes. At 0 V substrate voltages the fcc Pd lattice expands [Fig. 2]. The hydrogen incorporation takes place discontinuously and produces two different phases, both of which contain palladium metal atoms in a face centered cubic lattice (rock salt structure type). At room temperature PdH_x may contain two crystallographic phases, α and β. The α-phase exists at $x < 0.017$ whereas the β-phase is realized for $x > 0.58$ [4]. At −50 V substrate voltage only the hydrogen enriched palladium hydride is produced. Compared to the 0 V samples, the X–ray line profile of the −50 V samples is drastically changed. The X-ray line profiles of the as-deposited and also the 0 V treated films are characterized by a very high density of structure faults and/or by small particle sizes. The Pd (111) integral intensity is $I_{area} = 292$ cps, the integral width is $\beta = 1.27$. However, the −50 V treated films exhibits a reduced defect density and/or increasing particle sizes [Fig. 3]. The intensity increases to $I_{area} = 477$ cps and the integral width decreases to $\beta = 0.69$.

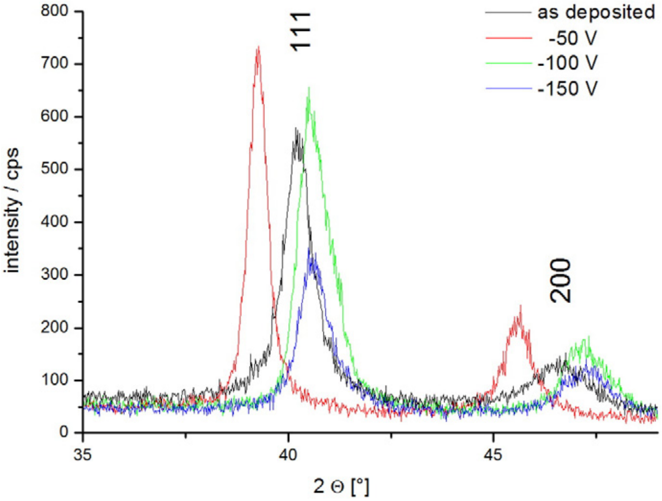

Fig. 1. X-ray patterns of fcc Pd films as deposited and treated with Ar/H_2 plasma at different substrate voltages after 30 min plasma exposure.

Hydrogen in d-metals is almost incompressible [15,16]. For Ni and Pd holds the volume change per hydrogen atom $\Delta\nu_H = 0.0025$ nm^3. If $\Delta\nu_H = $ const, the volume change in the fcc unit cell ΔV/V caused by N_H hydrogen atoms depends linearly on the hydrogen concentration $c_H = N_H / N_{Me}$. N_{Me} is the number of metal atoms. Then:

$$\frac{\Delta V}{V} = \frac{c_H}{V} \cdot N_{Me} \cdot \Delta\nu_H \qquad \text{with } \Omega = V/N_{Me}. \tag{1}$$

Vegard's rule holds:

$$c_H = \frac{\Delta V \cdot \Omega}{V \cdot \Delta\nu_H}. \tag{2}$$

Fig. 4 shows the lattice parameters of PdH_x after plasma exposure at 0 V and −50 V. The reference values for PdH_x (black points) were taken from [17]. If we assume Vegard's rule holds we get hydrogen concentrations of $c_H = 0.14$ and $c_H = 0.57$ for the produced palladium hydrides.

$PdH_{0.57}$ decomposes at temperatures >300 °C to form metallic fcc Pd [Fig. 5]. The hydrogen removal causes once again a decrease of lattice

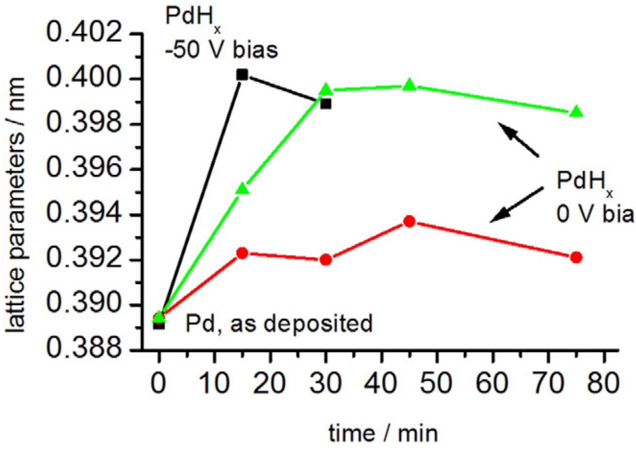

Fig. 2. Lattice parameters calculated from (111) reflections of fcc PdH_x after plasma exposure; substrate voltages 0 V and −50 V.