Influence of Ar/H_2 Plasma on Thin Palladium Films

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The effect of low energy plasma species onto solid surface layers is one focus of plasma research. We have found a new reaction pathway for synthesis of stable nickel hydride compounds under soft plasma conditions [1,2]. Most binary metal hydrides are synthesized by solid gas reactions between metal and hydrogen. In opposite to metallic nickel which forms hydrides only under high hydrogen pressure [3] palladium take up hydrogen easily under ambient pressure and temperature [4]. The formation of stable Pd hydrides under vacuum conditions at temperatures of 250 °C is not yet described to the best of our knowledge. In 1993, Fukai and Ökuma [5] discovered that gradual lattice contraction took place when Pd specimens were placed under high H_2 pressures and temperatures (5 GPa, 800°C). The formation of defect structures with vacancy-hydrogen (Vac-H) clusters is now recognised as one of the fundamental properties of M-H alloys. [6, 7].

In analogy to the experiments performed with thin metallic nickel films in Ar-H_2 plasmas [see also that report, 1,2] we have studied the behaviour of Pd layers in a microwave plasma. 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, 40 Pa working pressure without substrate heating. The energy influx to the film was changed by variation of the substrate bias in steps of 25 V from 0 V to -150 V.

To obtain insights into the chemical reactions and phase formation in these thin palladium films after Ar-H_2 plasma exposure grazing incidence measurements at HASYLAB beamline D4 (E = 10 keV) at DESY were performed using in-plane geometry. The measured Q-values range from 1 to 6 $Å^{-1}$.

The diffraction pattern consists of two sets of peaks labelled red: Pd-vac and blue: $PdH_{1.33}$ arising from to coexisting phases (Fig. 1). Pd-vac having a fcc structure with a = 3.874 Å is assigned to Pd with defect structure. The as deposited fcc Pd has a lattice constant a = 3.893 Å. The crystal structure of the second phase $PdH_{1.33}$ seems to be primitive cubic (SG: Pm-3, with a = 2.995 Å) [8].

In contrast to high pressure reactions of hydrogen with metallic Ni or Pd under plasma exposure we do not observe solid solutions over a wide range of hydrogen concentration. The hydrogen incorporation in Pd films also takes place discontinuously. At 0 V and -50 V bias voltage palladium hydride is formed stepwise up to a stoichiometry of $PdH_{0.7}$ (fcc).

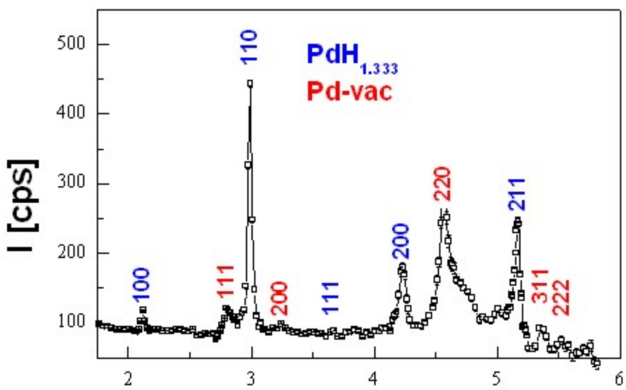
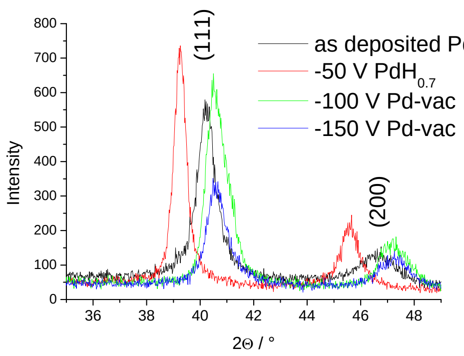


Fig.1: diffraction pattern taken after 45 min Ar-H_2 plasma exposure at -150 V bias voltage, at D4.



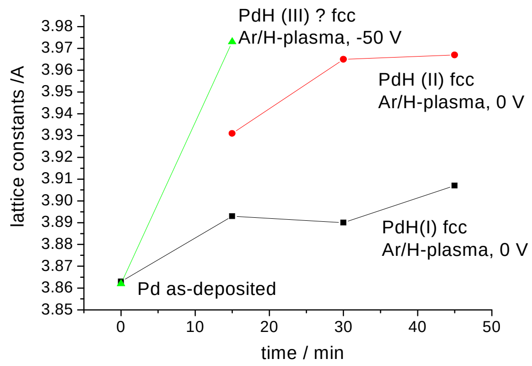


Figure 2: at home GIXD measurements of Pd films treated with Ar-H_2 plasma for 10 min at different bias voltages.

Figure 3: lattice constants of different palladium hydride phases. The exact hydrogen content is still unknown.

Our measurements in Greifswald show that the lattice constants increase from Pd to $PdH_{0.7}$ as shown in Fig. 2 and 3. However, bias voltages of -100 V and -150 V cause a shrinking of the unit cell in two steps (Fig. 2 and 4). We postulate the formation of vacancy hydrogen clusters [7]. In a second step cubic $PdH_{1.33}$ [8] is formed under long time plasma exposure, as was confirmed by experiments at D4.

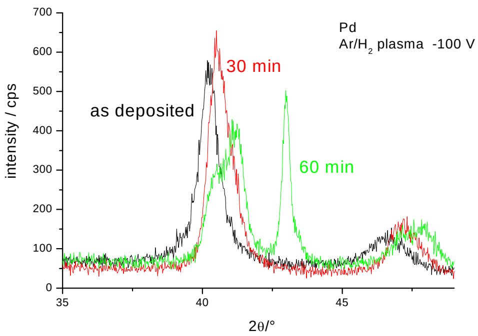


Figure 4: formation of lattice defects in Pd by plasma treatment at -100 V bias voltage and subsequent formation of $PdH_{1.33}$ (measured at home).

In analogy to the synthesis of nickel hydrides we have found different palladium hydride under low temperature plasma conditions. If the principle is applied to other 8b metals, it may be possible to form more stable metal hydride by plasma solid chemistry.

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