Letter

Evidence for a superstructure in hydrogen-implanted palladium

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Abstract

An alternative route for hydrogenation has been investigated: plasma-based ion implantation. This treatment applied to the Pd–H system induces a re-ordering of the metal lattice and superstructure lines have been observed by grazing incidence X-ray diffraction. These results are similar to those obtained by very high-pressure hydrogenation of palladium and prompt us to suggest that plasma-based hydrogen implantation is likely to induce superabundant vacancy phase generation.
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1. Introduction

Hydrogen may be reversibly inserted at normal pressure and ambient temperature in many intermetallic compounds leading to interstitial compounds (hydrides) whose structural, chemical and physical properties are strongly modified upon hydrogen insertion. In the case of palladium as in many metal-hydrogen systems, two hydrogenated phases are present in the phase diagram at 1 atm [1]: α, which dissolves 8 at.% H ($[H]/[Pd] \approx 0.09$) at room temperature; and β, which can dissolve from ~34 to ~42 at.% H ($[H]/[Pd]$ from ~0.51 to ~0.72). High pressure gas-phase charging allowed to reach the ratio $[H]/[Pd] = 1.0$ [2]. Atomic ratios ($[H]/[Pd]$) equal or higher than one are rather difficult to obtain by electrolytic method. Brand et al. [3] have obtained a very unstable phase with $[H]/[Pd] > 1.2$. Ion implantation of deuterium (D) into Pd was reported to produce concentrations as high as 1.3 to 1.6 D atoms per metal atom [4,5]. Other hydrogenated phases may be produced in both systems by high-pressure hydrogenation. An interesting case is that of hydrogen-induced vacancy phases for which hydrogen desorption is accompanied by a reconstruction of the starting network. In a pioneering work, Fukai [6] discovered that a large number of vacancies amounting up to 20 at.% were formed in Pd at high temperatures and very high hydrogen pressures. We have been able to reproduce these results and to stabilize the superabundant vacancy phase at room temperature and normal pressure [7]. Oates and Wenzel [8] has commented, the results obtained by Fukai [6] and inferred that an atomic ratio $[H]/[Pd] \approx 1.2$ must have been reached in their experiments.

In the present work, thin foils of palladium were hydrogenated by plasma-based ion implantation (PBII). The material was then characterized by X-ray diffraction.

2. Experimental

High purity annealed palladium thin foils (0.14 mm) were subjected to plasma-based ion implantation of hydrogen. An attractive method to introduce hydrogen in the near surface region of any material is ion implantation. In conventional ion implantation, an ion source is used to create an ion beam of the species to be implanted. Then, the ion beam is accelerated and transported to the substrate. Since the spot size is usually smaller than the substrate size, mechanical or electrostatic scanning are used to achieve dose uniformity.

In 1987, a new process, so-called plasma-based ion implantation (PBII), was developed to circumvent the beam line restrictions [9]. In the PBII technique, substrates are

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immersed directly in the plasma and are biased with high negative voltage pulses. The ions present in the plasma are thus accelerated towards the substrate surface where they are implanted.

The implantation of hydrogen has been performed in a distributed electron cyclotron resonance (DECR) plasma reactor previously described [10,11]. The plasma parameters obtained in an argon 10%–hydrogen 90% gas mixture at a total pressure of 0.33 Pa and 1.8 kW microwave input power (2.45 GHz) are the following: electron temperature $kT_e = 1.0$ eV, plasma potential $V_p = +6.5$ V, floating potential $V_f = +4.0$ V, and plasma density $n = 8.0 \times 10^9$ cm^{-3}. The hydrogen ion distribution in pure hydrogen plasma, as measured by mass spectrometry [12], is 78% for H$^+$ ions and 22% for H$_2^+$ and H$_3^+$ ions. This plasma parameter is quite important since H$^+$, H$_2^+$, and H$_3^+$ ions, accelerated onto the substrate under the same voltage difference, are implanted in the substrate at three distinct projection depths. Of course, in an argon–hydrogen mixture, Ar$^+$ ions are also present in the plasma. The role of argon is to help sustaining the hydrogen-based discharge and cleaning the substrate surface (carbon and oxygen desorption) in between the high voltage pulses.

The 100 kV/100 A pulse generator used for substrate biasing [13] can deliver high-voltage high-current negative pulses with a maximum frequency $f = 50$ Hz. The pulse duration is fixed at $\tau = 38$ μs and the pulse frequency at its maximum value 50 Hz. Therefore, the total dose (cm^{-2}) implanted in nickel and palladium is proportional to the total processing time t or the cumulated time T of high voltage pulses $T = \tau \times f \times t$. During PBII processing, the substrate-holder is cooled with a circulation of insulating oil, so that the substrate temperature never exceeds 200 °C under the operating conditions mentioned above. The two relevant parameters of this process are then the pulse voltage V_0 and the effective time T of implantation.

In this experimental study, the Ni and Pd samples have been implanted with ion energies of 40 keV, corresponding to a pulse voltage of $V_0 = -40$ kV. The implantation time $T = 12$ s corresponds to a processing time $t = 106$ min. In

the absence of calibration, the value of the implanted dose can be estimated to be of the order of 5×10^{16} cm^{-2}. Using the program TRIM 95 [14], the calculated implanted depths for 40 keV H$^+$ ions in Pd and Ni are 201 and 199 nm, with standard deviations ΔR_p of 80 and 52 nm, respectively. The corresponding values for 40 keV H$_2^+$ ions in Pd and Ni are 115 and 113 nm, with standard deviations ΔR_p of 54 and 39 nm, respectively. For 40 keV Ar$^+$ ions, the implanted depths R_p in Pd and Ni are only 23.4 and 17.9 nm with standard deviations ΔR_p of 13.5 and 9.1 nm, respectively.

3. Results and discussion

The X-ray diffraction patterns were collected as a function of the incidence angle in the grazing incidence domain. The near surface region was thus investigated and superstructure lines were detected as shown in Fig. 1. These lines could be easily indexed as (1 0 0) and (1 1 0) of a primitive cubic lattice with a parameter of about 3.9 Å.

It is interesting to compare these results with those obtained in the case of very high pressure gas-phase charging. Application of high pressure on the Pd foil generates defects such as dislocations, which are accommodated by the lattice through a shear mechanism. The same kind of treatment at 800 °C with hydrogen leads to a simple cubic phase with a contracted lattice indicating a vacancy-containing phase. The ordering is of Cu$_3$Au-type and has been ascribed to the presence of vacancies, thus leading to the formula Pd$_3$($\square$H$_x$) [15]. In the present case, the observed symmetry lowering (face centered cubic to primitive cubic) is of a similar type and corresponds to an ordering within the metal lattice since the X-ray scattering cross-section of hydrogen is negligible compared to that of palladium. When using the grazing incidence XRD technique, refraction effects are significantly important at angles close to the refraction limit angle and lead to a slight shift of the diffraction lines. It is then rather difficult to extract accurate lattice parameters from the available data. In particular, it is not possible to detect the contracted-lattice state from the current data.
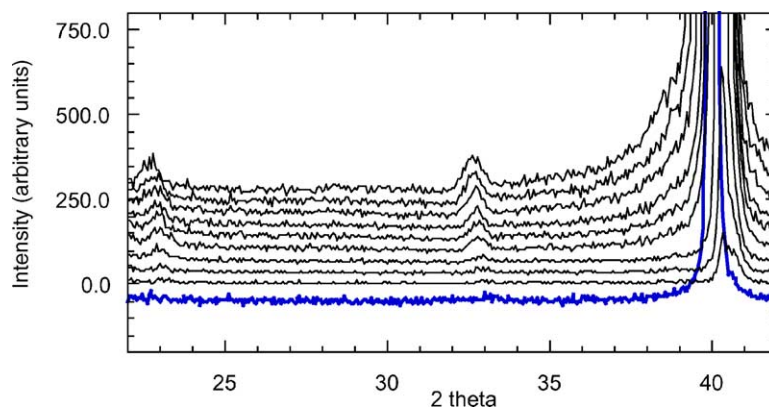

Fig. 1. Grazing incidence XRD patterns of the plasma beam hydrogen-implanted Pd in the near surface region. In bold: the same region before implantation.
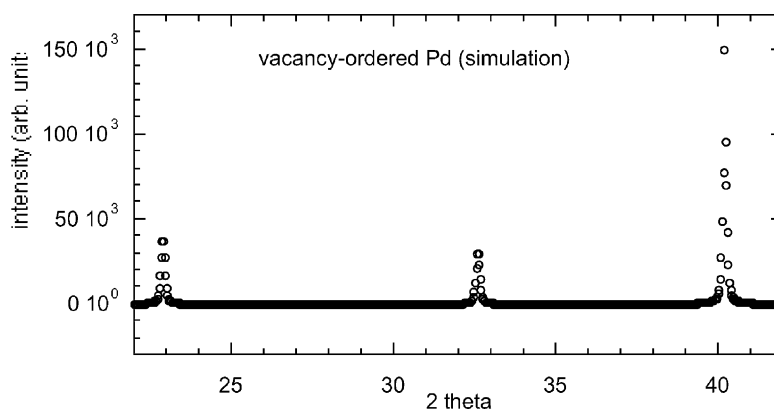
Fig. 2. Calculated diffraction pattern for $Pd_3\square$, assuming $L1_2$ structure.

Another interesting feature of the X-ray diffraction patterns is the detectable peak broadening that increases as the investigated depth is varied, it is associated with strain effects. This peak broadening may be also indicative of varying vacancy concentration as a function of investigated depth; this is also sensible since the peak intensity is observed to vary with the incidence angle that is the explored depth.

Although the origin of the superlattice lines cannot be fully understood with the set of available experimental data, we propose that a vacancy-ordered structure (of Cu_3Au-type) is formed in the fcc lattice. This assumption is supported by the computed diffraction pattern shown in Fig. 2.

In this computation, the modeling fairly reproduces the intensity of the superstructure lines and thus corroborates the cluster model (octahedral) proposed by Fukai in agreement with a vacancy concentration of 20%. It is worth noticing that the current data give support to the expectation of Fukai [16] regarding the generation of superabundant vacancies in hydrogen-treated metals.

4. Conclusion

It has been shown that hydrogenation of palladium using the plasma-based ion implantation technique induces a reordering of the fcc metal lattice. Strong hints suggest formation of a vacancy-ordered structure and show thereby that very high pressure hydrogenation is not mandatory to induce superabundant vacancy phase generation.

Plasma-based ion implantation appears to be a promising and fairly effective route for hydrogenation, additional experiments and characterizations are in progress.

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