Effect of hydrogen on the atomic structure of Pd(001)

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The atomic structures of clean and hydrogen-adsorbed Pd(001) are investigated by low energy electron diffraction (LEED) I/V analysis. Clean Pd(001) shows little surface relaxation in sharp contrast to previous reports. Adsorbing 1 monolayer of hydrogen on Pd(001), we observe sizable expansion of the interlayer spacing of the first two surface layers, $d_{12}$ by 4.7% of the corresponding one of bulk Pd. Both experimental observations are in excellent agreement with the predictions of recent ab initio calculations. A series of experiments with varying coverages of hydrogen adsorbed on Pd(001), reveals that $d_{12}$ monotonically increases with the increasing coverage. Such an observation strongly supports the contention that the previous observation of expanded $d_{12}$ in clean Pd(001) results from contamination of the surface by residual hydrogen.

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I. INTRODUCTION

Hydrogen is well known to diffuse and dissolve well in Pd, which has motivated researchers from many different disciplines to investigate Pd-H complex due to its possible application as hydrogen carrier. The adsorption, dissociation and diffusion of hydrogen on single crystalline Pd has been studied as a model system to understand atomistic process of hydrogen incorporation and catalytic behavior of Pd. For Pd(001), numerous experimental works have been performed by employing low energy electron diffraction (LEED), He ion scattering, work function measurement, thermal desorption spectroscopy (TDS), nuclear reaction analysis (NRA), electron energy loss spectroscopy (EELS), and thermal desorption spectroscopy (TDS). Moreover, ab initio calculations have been made to study electronic and atomic structures, and chemical properties of Pd(001) upon hydrogen adsorption. Thereupon, found are many physical and chemical properties of Pd(001) such as dissociation mechanism of $H_2$, adsorption sites and adsorption energies of hydrogen, dependence of work function on the coverage of hydrogen, desorption and dissociation kinetics of hydrogen on Pd(001).

The atomic structure of clean and hydrogen-adsorbed Pd(001) is, however, not established yet. Behm et al. and Jona et al. pointed out two possibilities; magnetization of the surface and hydrogen contamination of Pd(001). Magnetization of Pd thin (< 5ML) films grown on Ag(001) and Au(001) was investigated by MOKE, but null magnetization is found. Both self-consistent tight binding calculation and ab initio calculation by full potential linearized augmented plane wave method (FLAPW) predicted delicate dependence of magnetization of Pd on the thickness of slab to model Pd(001). (Note: at the moment we are waiting for the result of Prof. Hong on the effect of magnetization on surface relaxation of Pd(001). He suggested very small, if any, relaxation due to the tiny magnetization of Pd.) On the other hand, for hydrogen covered Pd(001), expansion of $d_{12}$ is predicted. However, no direct experimental investigation has been made yet to examine the correlation between hydrogen coverage and the atomic structure of Pd(001). Such study should be critical to identify the origin of the observed expansion of $d_{12}$.

The present work is aimed to experimentally clarify the effect of hydrogen coverage on the atomic structure of Pd(001). We carefully prepare Pd(001) with various hydrogen coverages, and investigate their atomic structure by LEED I/V analysis. From that study, we find that there is little expansion of $d_{12}$ for clean Pd(001), while the $d_{12}$ monotonically expands with increasing hydrogen coverage. We also find that the remnant hydrogen in our experimental chamber, although its base pressure is very low, low $10^{-11}$ mbar, can swiftly contaminate Pd(001) and result in the notable expansion of $d_{12}$. Combining all the abovementioned observation, we conclude that expansion of $d_{12}$ of clean Pd(001) previously reported by other experimental groups originates from hydrogen contamination of Pd(001).
II. EXPERIMENTS AND LEED I/V ANALYSIS

A. Experiment

All the experiments were performed in an ultrahigh vacuum chamber with its base pressure low $10^{-11}$ mbar. The chamber was equipped with rear-view LEED optics and cylindrical mirror analyzer for Auger electron spectroscopy (AES). Pd(001) sample was of "top-hat" shape with its diameter, 8 mm, and thickness, 1 mm. We cleaned the sample by iterating sputtering with 2 KeV Ar$^+$ and annealing at 950 K for 20 minutes. To remove remnant carbon, we oxidized it by annealing the sample at 650K in an oxygen ambient pressure of $1 \times 10^{-8}$ mbar, and desorbed it at 950 K, until there was observed no AES peak of carbon. Once the contaminants were removed of the sample, we prepared the sample by sputtering and annealing only for once. From now on, we call this routine sample preparation procedure, standard procedure.

For the standard procedure, the time required to complete acquisition of I/V spectra was around 2 hours from the start of annealing. During that period, it seemed highly possible that the surface was contaminated by residual hydrogen. Thus, we prepared clean sample in two different ways to ensure cleanliness of Pd(001). The first way was to minimize the time till I/V acquisition; After following the standard procedure, we flashed the sample up to 950 K to detach any residual hydrogen and cooled the sample to 150 K within 30 minutes by liquid nitrogen. (Desorption temperatures of surface and subsurface hydrogen, $T_D$, were known to be lower than 340 K[6] Following this rapid cleaning process, we could finish the I/V acquisition within 1 hour in the better vacuum condition. The second method was based on the fact that the desorption temperature of hydrogen was around 340 K; We took I/V with the sample at temperatures higher than the desorption temperature.

Hydrogen covered Pd(001) was also investigated as follows; After flashing the sample at 950 K, we cooled it down to 150 K for hydrogen dose, because the hydrogen was known to dissolve into bulk Pd near room temperature[6,7] We dosed 6~12 Langmuir (L) of hydrogen in an ambient hydrogen pressure, $1 \times 10^{-8}$ mbar. Since there was little difference in LEED I/V for dosing more than 6 L of hydrogen, we concluded that 6 L of hydrogen was enough to saturate Pd(001). Hydrogen saturated Pd(001) showed $p(1 \times 1)$ LEED pattern with its background intensity about the same as for clean Pd(001) on visual inspection.

B. LEED I/V Analysis

LEED I/V spectra were obtained by a fully automated video-LEED system comprised of a charge coupled device (CCD) camera and a program for image processing. The I/V spectra were always taken with the sample normal to the electron beam. LEED I/V analysis was made by SATLEED program[18] Scattering phase shifts were obtained from potentials of Moruzi et.al[19] for its angular momentum, $l$ from 0 to 10. Thermal vibration effect was taken into account by Debye-Waller factor with Debye temperatures of H and Pd, 1800 K and 260 K, respectively. We also varied the Debye temperatures as fitting parameters, however, the best-fit atomic structure was not sensitive to them. The quality of I/V fit was judged by the reliability factor of Pendry, $R_p$, and error limit was set by its variance[20] Fitting was made for various model structures, and the best-fit structure was concluded after iterating the fitting till the difference between the input structural parameters and those of the resulting best-fit structure were within 0.001 Å.

III. RESULTS AND DISCUSSION

In Fig. 1, shown are LEED I/V spectra for $[1,0]$, $[1,1]$, $[2,0]$, $[2,1]$, $[2,2]$, $[3,0]$ beams of the rapidly cleaned Pd(001). The total energy range of the spectra is 2468 eV. In Table I, summarized are the best-fit structures for three, most conceivable models, given the present experimental condition and the results in literatures. The minimum R-factor is found for clean Pd(001) model and is very small, 0.17, in regards to the large number of beams and extensive energy range of I/V spectra. The theoretical I/V spectra of the best-fit structure in Fig.1 well reproduces most features in the experimental spectra, which purports the present I/V fitting reliable. $R_p$-factors for the other models, some of which are given in Table I, are outside the variance of the minimum $R_p$-factor of clean Pd(001), and thus they are excluded for the model of rapidly cleaned Pd(001).

![FIG. 1: LEED I/V spectra for rapidly cleaned Pd(001). Thick line is experimental curve and the dotted line is theoretical one.](image-url)
The best-fit structure for rapidly cleaned Pd(001) shows little surface relaxation (Table I): $d_{12}$ shows a negligible amount of expansion by $+0.2\%$ of $d_B$. (From now on, all structural variation is given with respect to $d_B$.) $d_{12}$ for clean Pd(001) is predicted to contract by less than $1\%$ by recent theoretical works ignoring spin-polarization effects, which is in good agreement with the present experimental result. Hence, it is likely that the rapidly cleaned sample is really clean Pd(001).

The atomic structures of both hydrogen-adsorbed and subsequently hydrogen-desorbed Pd(001) are also investigated by LEED I/V analyses. The I/V spectra are obtained after dosing 6 L of hydrogen on Pd(001) at 150 K and then while gradually warming the sample beyond $T_D$. Detailed sample preparation procedure is as described in the experiment section.

In the beginning, the atomic structure of hydrogen-adsorbed Pd(001) at 150 K is investigated by the analyses of LEED I/V spectra for [1.0], [1.1], [2.0], [2.1] beams with their total energy range, 1810 eV. Table II is a summary of the I/V analysis. The best-fit is found for a model where 1 monolayer (ML) of hydrogen is adsorbed on the four-fold hollow site of Pd(001). (Fig. 2) We find that the theoretical I/V spectra for the best-fit structure well reproduce all the experimental features in Fig. 3. The $R_p$-factor of the best-fit structure is also quite low, 0.1626, and the other structures result in $R_p$-factors far beyond the variance of the minimum $R_p$-factor (Table II), assuring that the best-fit structure represents the atomic structure of the hydrogen-adsorbed Pd(001).

For the best-fit structure (Fig. 2 and Table II), the distance between hydrogen and Pd surface layer, $d_H$, is 0.2 Å. Large error limit of $d_H$ reflects small scattering cross section of hydrogen. $d_{12}$ expands by 4.7\%, and $d_{23}$ and $d_{34}$ show no relaxation. The present observation is in excellent agreement with recent theoretical predictions that four-fold hollow site is the energetically most favored adsorption site of hydrogen till its coverage reaches 1 ML, and $d_H$ is $0.1 \sim 0.25$ Å, and $d_{12}$ expands by $4.4 \sim 5.2\%$. Besides, ion-channeling experiments predict $d_H$ to be 0.3 Å. In this experiment, $d_H$ includes $\Delta d_{12}$, the variation of $d_{12}$ from $d_B$. If we also include $\Delta d_{12}$ to $d_H$, the resulting value is 0.29 Å, in excellent agreement with the result of ion-channeling experiment, 0.3 Å.

We trace the evolution of its surface structure by LEED I/V analysis while gradually annealing the sample to temperatures higher than $T_D$, since we expect to obtain clean Pd(001) by desorbing hydrogen from the sample. In Table III, below 340 K, the best-fit model

| Theory | Experiment |
|--------|------------|
| LDA    | Clean Hollow-H | 150-310 K |
| GGA    | Subsurface-H | (Jona) |
| $\Delta d_{12}/d_B$ | +2.2 $\%$ | +2.4 $\%$ |
| $\Delta d_{23}/d_B$ | +0.3 $\%$ | +1.2 $\%$ |
| $R_p$-factor | 0.1944 | 0.1941 |

![FIG. 2: The best-fit structure of nominal 1 ML of hydrogen covered Pd(001).](image)

![FIG. 3: LEED I/V spectra for the nominal 1ML of hydrogen covered Pd(001). Solid line signifies theoretical result and the doted one does theoretical spectra for the best-fit structure.](image)
is Pd(001) with 1 ML of hydrogen adsorbed on fourfold hollow site. Further, $d_{12}$ and $d_{23}$ are maintained around the same value as that at 150 K. If the sample temperature ($T_S$) is raised higher than $T_D$, the best-fit model switches from hydrogen-adsorbed Pd(001) to clean Pd(001) (Table III), and both $d_{12}$ and $d_{23}$ simultaneously show such abrupt contraction as demonstrated in Fig. 4. Although the $R_P$-factors of both structures are within the variance of the minimum R-factor, such an observation of the change of the best-fit structure is consistent with the observation of hydrogen desorption at 340 K. The $\Delta d_{12}$ for $T_S$ higher than $T_D$, is $+0.6$--$0.9 \%$, which is in good agreement with that found for the rapidly cleaned Pd(001). From the agreement of the atomic structures of the two differently prepared clean Pd(001), we conclude that clean Pd(001) must have almost the bulk-terminated structure, while hydrogen-adsorbed Pd(001) shows notable expansion of the $d_{12}$.

Although clean Pd(001) found in the present experiment show little surface relaxation, previous experiments report the expansion of $d_{12}$ by 2.5 \% to 3 \%. The observation of the expansion of $d_{12}$ upon hydrogen adsorption suggests that the previous experiments were performed with hydrogen-contaminated Pd(001). For the direct examination of such possibility, we perform the sample preparation and the I/V acquisition in the standard way without making extra-efforts such as flash cleaning and rapid cooling as made in the rapid cleaning procedure. This experiment may correspond to a replication of previous experiments.

In Table IV, given is a summary of I/V analyses for Pd(001) cleaned via the standard procedure. The most notable result is that $d_{12}$ increases by 1.8 \% (Also, see Fig. 5), which clearly contrasts to the almost bulk-terminated structure of clean Pd(001). $d_{12}$ in the present experiment, however, expands less than in previous reports, 2.5 \% to 3 \%. The reason why different amount of expansion of $d_{12}$ is observed experiment by experiment is supposed to be different degree of hydrogen contamination resulting from different base pressure and duration of experiment. To directly examine this conjecture, we dose varying amounts of hydrogen on Pd(001) at room temperature, and investigate the dependence of the atomic structure on hydrogen dosage by LEED I/V analysis.

In Table IV, given are the best-fit structures of Pd(001) 1) prepared via standard cleaning and 2) dosed respectively by 6 and 12 L of hydrogen at room temperature.

### Table II: Results of LEED I/V analyses for H-adsorbed Pd(001) at 150 K. $d_{12}$ and $d_{12}$ are as defined in Fig. 2. Among others, four most relevant model structures, Pd(001) with hydrogen at fourfold hollow site, Hollow-H, Bridge-H, On-top -H, and Clean signify structures where 1 ML of hydrogen is adsorbed respectively on four-fold hollow site, bridge site, and on-top site, and clean Pd(001).

| Model structure | $d_H$ (Å) | $\Delta d_{12}/d_B$ (%) | $R_P$-factor | $\Delta d_{23}/d_B$ (%) | $R_P$-factor |
|-----------------|----------|------------------------|--------------|------------------------|--------------|
| Hollow-H        | 0.20 ±0.02 | +4.7 ±1.1 %           | 1.21 Å       | +5.2 %                 | 1.10 Å       |
| Bridge-H        | 0.21 ±0.09 | +0.6 ±0.9 %           | 0.1626       | -1.0 %                 | 0.2720       |
| On-top-H        | 0.20 ±0.09 | -1.0 %                 | 0.3594       | -0.1 %                 | 0.3594       |
| Clean           |          |                        | 0.2646       |                        |              |

### Table III: After adsorbing 1 ML of hydrogen on Pd(001) at 150 K, temperature of the sample is gradually raised to 340 K, during which LEED I/V spectra are taken and analyzed. Hollow-H signifies a model, 1 ML of hydrogen adsorbed the four-fold hollow site of Pd(001), and Clean does clean Pd(001).

| Exp. temp. (K) | $d_H$ (Å) | $\Delta d_{12}/d_B$ (%) | $R_P$-factor | $\Delta d_{23}/d_B$ (%) | $R_P$-factor |
|----------------|----------|------------------------|--------------|------------------------|--------------|
| 220 K          | 0.20 Å   | +4.5 %                 | 0.1692       | +5.3 %                 | 0.2582       |
| 250 K          | 0.20 Å   | +4.4 %                 | 0.1748       | +5.2 %                 | 0.2658       |
| 280 K          | 0.21 Å   | +4.4 %                 | 0.1826       | +5.2 %                 | 0.2733       |
| 310 K          | 0.21 Å   | +4.2 %                 | 0.2088       | +5.1 %                 | 0.2931       |
| 340 K          | 0.44 Å   | +0.5 %                 | 0.2007       | -0.9 %                 | 0.2004       |
| 400 K          | 0.33 Å   | +0.6 %                 | 0.1956       | +0.6 %                 | 0.1873       |
| 430 K          | 0.61 Å   | +0.7 %                 | 0.2043       | +0.8 %                 | 0.1899       |

### Table IV: Summary of I/V analyses for Pd(001) cleaned via the standard procedure. The most notable result is that $d_{12}$ increases by 1.8 \%. (Also, see Fig. 5), which clearly contrasts to the almost bulk-terminated structure of clean Pd(001). $d_{12}$ in the present experiment, however, expands less than in previous reports, 2.5 \% to 3 \%. The reason why different amount of expansion of $d_{12}$ is observed experiment by experiment is supposed to be different degree of hydrogen contamination resulting from different base pressure and duration of experiment. To directly examine this conjecture, we dose varying amounts of hydrogen on Pd(001) at room temperature, and investigate the dependence of the atomic structure on hydrogen dosage by LEED I/V analysis.

| Exp. | $d_{12}$ (Å) | $d_{23}$ (Å) | $\Delta d_{12}$ (Å) | $\Delta d_{23}$ (Å) |
|------|--------------|--------------|----------------------|---------------------|
| 6 L  | 0.16 Å (hollow) | 0.20 Å      | +5.2 %              | +0.2 %              |
| 12 L |              |              | (d$_H$ + $\Delta d_{12}$) |              |
TABLE IV: LEED I/V analyses are made for Pd(001) cleaned via standard procedure, and for 6 (6L−H) and 12 L (12L−H) of hydrogen-dosed Pd(001). Respective I/V is fit, assuming clean Pd(001) to compare with previous results.

|          | $\Delta d_{12}/d_B$ | $\Delta d_{23}/d_B$ | $R_B$-factor |
|----------|---------------------|---------------------|--------------|
| standard | +1.8 %              | -0.7 %              | 0.1944       |
| 6L−H     | +2.4 %              | -0.7 %              | 0.2095       |
| 12L−H    | +3.0 %              | -1.0 %              | 0.2235       |

When 6 L of hydrogen is dosed, $d_{12}$ expands by 2.4 %, while it does by 3.0 % with increased dosage of 12 L. In regards to the fact that $d_{12}$ expands by 4.7 % for hydrogen saturated surface at 150 K, we find monotonic increase of $\Delta d_{12}$ with increasing amount of hydrogen coverage. (Fig. 5) From the above account, the reason why the amount of expansion of $d_{12}$ varies experiment by experiment is evidently the different degree of hydrogen contamination due to different sample cleaning procedure and/or experimental environment. In short, the previous experimental results of expanded $d_{12}$ of clean Pd(001) is attributed to the contamination by residual hydrogen.

IV. SUMMARY

We prepare clean Pd(001) in two different ways, rapid cleaning and hydrogen desorption, and consistently find by LEED I//V analysis that the atomic structure of clean Pd(001) is similar to bulk-terminated Pd(001). (Fig. 1 and 4) On the other hand, hydrogen covered surface shows monotonic increase of $d_{12}$ with increasing hydrogen coverage. (Fig. 5) The present, systematic study on the effect of hydrogen on the atomic structure of Pd(001) firmly conclude that the previously reported expansion of interlayer spacing of Pd(001) originates from hydrogen contamination of the sample.

Acknowledgments

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