Acceleration of hydrogen absorption by palladium through surface alloying with gold

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Enforcement of hydrogen (H) absorption kinetics improves the performance of hydrogen-purifying membranes and hydrogen-storage materials, which is necessary for utilizing hydrogen as a carbon-free energy carrier. Pd–Au alloys are known to show higher hydrogen solubility than pure Pd. However, the effect of Au on the hydrogen penetration from the surface into the subsurface region has not been clarified so far. Here, we investigate the hydrogen absorption at Pd–Au surface alloys on Pd(110) by means of thermal desorption spectroscopy (TDS) and hydrogen depth profiling with nuclear reaction analysis (NRA). We demonstrate that alloying the Pd(110) surface with submonolayer amounts of Au dramatically accelerates the hydrogen absorption. The degree of acceleration shows a volcano-shaped form against Au coverage. This kinetic enhancement is explained by a reduced penetration barrier mainly caused by a destabilization of chemisorbed surface hydrogen, which is supported by density-functional-theory (DFT) calculations. The destabilization of chemisorbed surface hydrogen is attributed to the change of the surface electronic states as observed by angle-resolved photoemission spectroscopy (ARPES). If generalized, these discoveries may lead to improving and controlling the hydrogen transport across the surfaces of hydrogen-absorbing materials.

Significance

Surfaces are gates to control the transport of energy and materials between the gas phase and bulk. For the hydrogen storage, the transport of hydrogen across the surface is recognized as the bottleneck, e.g., 1 H\textsubscript{2} in 1,000 impinging a Pd surface penetrates the surface. Here, we demonstrate that alloying the Pd(110) surface with submonolayer amounts of Au dramatically accelerates the hydrogen absorption, by a factor of more than 40. This discovery will lead to enhancement of hydrogen absorption kinetics, thereby improving the performance of hydrogen-purifying membranes and hydrogen-storage materials, which is a key for utilizing hydrogen as a carbon-free energy carrier.

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the intensity of the $\alpha_1$ peak is higher than that for clean Pd(110), while the $\beta$-peak intensity is about 35% of that from pure Pd(110). The peak temperature of the $\beta$ feature is 272 K here, but shifts to lower temperature when the Au amount is increased as shown in Fig. 1B. The peak temperature of the $\alpha_1$ peak shifts to higher temperature as the peak intensity increases and the peak shape is asymmetric with a sharp high-temperature edge, which are typical features of zero-order desorption and characteristic for near-surface absorbed hydrogen in Pd (14, 16, 17).

To support the above assignment of the $\alpha_1$ TDS peak to absorbed H, hydrogen concentration depth profiles were measured by NRA. Fig. 2 shows the NRA profiles from the clean Pd(110) surface and the 0.3-ML Au/Pd(110) surface after 100-Langmuir H$_2$ exposure at 120 K. The NRA profile from the clean Pd(110) surface shows a Gaussian-like feature centered around depth 0 and a low-intensity decaying feature up to 10 nm. The Gaussian-like feature corresponds to the chemisorbed surface hydrogen and the decaying feature corresponds to the absorbed hydrogen into the near-surface region (6). The NRA profile from Au/Pd(110) shows a high $\gamma$-ray yield near the surface that decays into the depth up to 10 nm, which indicates substantial H incorporation into the near-surface region as well as chemisorption of H on the surface. The area of the profile taken from Au/Pd(110) is about 4.5× larger than that from bare Pd(110) in this depth region. Since the $\gamma$-ray yield at 10 nm is still higher than in pure Pd(110), hydrogen is expected to be absorbed in the deeper region than in pure Pd(110). The H concentrations at 5 nm for pure Pd(110) and the Pd–Au surface alloy are 4.2 and 13 at %, respectively. Since the $\beta$ peak is already saturated on pure Pd(110), the increased amount corresponds to the hydrogen absorbed in the near-surface region. The NRA data support the conclusion that the $\alpha_1$ peak in the TDS spectra, which increased significantly by addition of Au, originates from the absorbed hydrogen. Since the Au atoms mainly stay in the surface layer, Au only modifies the hydrogen solubility in a few subsurface layers and the hydrogen solubility below these layers should be nearly the same as in pure Pd(110). The NRA data on the other hand show that the H-containing region of Au/Pd(110) with a higher H concentration than Pd(110) extends beyond 10 nm. Therefore, the effect of Au is to modify the kinetics of penetration from surface to subsurface rather than to significantly influence the hydrogen solubility.

Fig. 3 shows the area of the $\alpha_1$ and $\beta$ peaks from the Au/Pd(110) surfaces normalized by those from Pd(110) as a function of the Au coverage. To determine individual peak areas, we separated the $\alpha_1$ and $\beta$ peaks by fitting the TDS spectra to two asymmetric Gaussian functions. The $\alpha_1$-peak area of the Au/Pd(110) surfaces shows a volcano-shaped form (18) against Au coverage with a maximum around 0.4-ML Au, from where it gradually decreases with increasing amount of Au. The $\alpha_2$-peak area is about 42$x$ larger at 0.4 ML and notably 2.3× larger at 2.2 ML compared with that from clean Pd(110). This result shows that the surface alloying with submonolayer amounts of Au significantly enhances the hydrogen absorption. Fig. 3 (Inset) shows the $\beta$-peak area normalized by that from Pd(110). The intensity of the $\beta$ peak monotonously decreases with increasing Au coverage.

It is recognized that the rate-limiting step for hydrogen absorption is the penetration from the surface to the subsurface region. Hydrogen atoms have to overcome the penetration barrier to diffuse from the surface into the subsurface region. The penetration barrier is determined by the energy levels at the adsorption state and the transition state to the first subsurface octahedral site. To clarify the origin of the accelerated hydrogen absorption, the adiabatic potential for a single H to penetrate the surface was calculated for the clean Pd(110) and 0.5-ML Au/Pd(110) surfaces by DFT calculations. Fig. 4 shows the atomic structure of the 0.5-ML Au/Pd(110) surface assumed for the calculation, where half of the surface Pd atoms of Pd(110) were periodically replaced by Au atoms. Fig. 4B shows the calculated energy diagrams from the surface site (surface octahedral site, O1) through the subsurface tetrahedral (T1, T2) and octahedral (O2, O3) sites. The calculated energy levels are shown with reference to the metal and...
Au coverage dependence of the $\beta$-peak area of Au/Pd(110) surfaces normalized by that from Pd(110) as a function of Au coverage. (Inset) $\beta$-peak area from the Au/Pd(110) surfaces normalized by that from Pd(110) as a function of Au coverage. Lines through the data points are guides to the eye.

With increasing surface Au concentration, the chemisorbed hydrogen surface hydrogen is expected to be accordingly destabilized. This destabilization also enhances $\text{H}_2$ desorption, which is a competitive process to the $\text{H}$ penetration process. The transition state from the surface to the O2 site will be also accordingly destabilized, which increases the penetration barrier. In addition, the number of surface Pd sites decreases and the $\text{H}_2$ dissociation barrier may appear, resulting in the lower adsorption rate. All these effects lower the absorption rate at higher surface Au concentrations. As a result, the enhancement factor of hydrogen absorption shows a volcano-shaped form with a maximum at a certain amount of Au as seen from the $\alpha_1$ TDS peak area in Fig. 3.

It should be noted that Fig. 4 shows the energy diagram for the direct penetration process where a H atom diffuses from the surface to the subsurface sites. However, it is reported that the hydrogen absorption might proceed in a concerted motion of two H atoms involving a chemisorbed H and an excess H atom supplied by dissociation of H$_2$ on the nearly fully H-covered surface (5, 6). In that case, a more detailed analysis including the interaction of these H atoms with the surface is required, which will be a future subject to be solved.

The adsorption energy of a molecule on a metal surface depends on the surface electronic structure. Fig. 5 shows plots of the ARPES intensity as a function of the electron momentum $k_y$ and electron energy $E$ with respect to the Fermi level $E_F$ ($E - E_F$) from Pd(110) and Au/Pd(110) surfaces measured along the surface Brillouin zone $\Gamma - Y$ line. For the clean Pd(110) surface, a sharp band is observed around 0.3 eV below $E_F$ as seen in Fig. 5A. The band shows a nearly flat feature near $k_y = 0$ and bends downward at $k_y > 0.4$ Å$^{-1}$. This band corresponds to the surface state or the quantum well state of Pd(110) as reported previously (20–23). An additional feature around 2–3 eV appears at $k_y > 0.6$ Å$^{-1}$. Fig. 5B shows the ARPES intensity taken from 0.48-ML Au/Pd(110). The intensity of the Pd-related band around 0.3 eV decreases while the intensity of the band around 2–3 eV at $k_y = 0$ increases. Fig. 5C shows the ARPES data from the as-grown 2.4-ML Au/Pd(110). The 0.3-eV band is completely absent and a broad band around 2–5 eV appears. There is also intensity...
around 6–7 eV. These bands around 2–5 and 6–7 eV correspond to the Au d bands and the flat region with a low intensity from $E_F$ to 2 eV corresponds to the Au s-p band as observed on Au surfaces and Au-rich Pd–Au surface alloys (24–26), indicating that the as-grown 2.4-ML Au/Pd(110) surface is similar to the Au surface. Therefore, the band around 2–3 eV near $k_y = 0$ observed in Fig. 5B is assigned to the Au band. The Au band around 2–3 eV shown in Fig. 5B is narrower and its position is shallower with respect to $E_F$ compared with that on the as-grown 2.4-ML Au/Pd(110) (SI Appendix, Fig. S2). The features of the 0.48-ML Au/Pd(110), which is an example of the Au/Pd(110) surface with submonolayer amounts of Au, look like a mixture of the bands from Pd(110) and Au(110) and resemble the features of the Pd$_{70}$Au$_{30}$(110) alloy surface with a surface Au concentration of 45–58% (11) shown in Fig. 5D.

It has been shown that the position of the metal d-band center with respect to $E_F$ is a good indicator of the adsorption energy of a molecule on a surface (27, 28). As the d-band center shifts downward away from $E_F$, the d-band center theory (27, 28) predicts that the surface becomes less reactive, resulting in a lower adsorption energy. As the d-band center shifts closer to $E_F$, on the other hand, the surface becomes more reactive, resulting in a higher adsorption energy. The ARPES data for the Au/Pd(110) surfaces with various amounts of Au show that the intensity of the Pd band decreases and its position shifts downward (SI Appendix, Fig. S2). On the basis of the d-band center model, this leads to destabilization of hydrogen adsorption on the surface Pd site. This explains the observed monotonic decrease in the peak temperature of the $\beta$ peak with increasing amount of Au (Fig. 1B).

Whereas the energies of O1, T1, and the transition state from O1 to T1 are destabilized on Au/Pd(110), which is well explained by the surface electronic structure, the energy level at the transition state from T1 to O2 is hardly changed and the energies of O2, T2, and the transition state from O2 to T2 are stabilized as revealed by the DFT calculations. This stabilization can be partly attributed to the expansion of the Pd lattice by Au that reduces the energy loss accompanied by the lattice distortion upon hydrogen absorption, which is used to explain the higher H solubility in Pd–Au alloys than in pure Pd.

In summary, we have investigated the hydrogen absorption by Au-alloyed Pd(110) surfaces, and found that the addition of submonolayer Au significantly accelerates hydrogen absorption. The enhancement factor shows a volcano-shaped form against Au coverage. This enhancement is explained by the destabilization of the chemisorbed surface hydrogen and the smaller increase of the energy level at the transition state of the penetration process compared with the surface, resulting in the decrease of the penetration barrier from the surface into the subsurface. Our results clearly show that the addition of only a small amount of Au can enhance the hydrogen absorption kinetics, which is important for the hydrogen storage and hydrogen purification. This finding will lead to improving and controlling the hydrogen transport across surfaces of Pd-related alloys and hydrogen-absorbing materials and also to controlling catalytic activities and selectivities of these surfaces for surface reactions where absorbed hydrogen plays important roles.

**Methods**

The experiments were performed in ultrahigh vacuum (UHV) chambers with a base pressure below 1 × 10$^{-8}$ Pa. A Pd single-crystal rod was Laue-oriented to the (110) direction, cut within 0.5° precision, and mechanically polished to submicrometer roughness with a suspension of Al$_2$O$_3$ powder (0.05-μm grain size). The Pd(110) sample was set in each UHV chamber and cleaned by repeated cycles of Ar ion sputtering at 300 K with an ion energy of 800 eV for 5 min, annealing at 1000 K in UHV, oxidation at 700–750 K in 5 × 10$^{-5}$ Pa O$_2$ for 4 min, reduction at 300 K in 5 × 10$^{-5}$ Pa H$_2$ for 1–4 min, and final flashing to 600 K in UHV. The surface of Pd(110) was characterized by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) (SI Appendix, Fig. S1).

The TDS measurements were performed at a heating rate of about 2 K s$^{-1}$ using a shielded and differentially pumped quadrupole mass spectrometer after exposure to H$_2$ by backfilling the chamber through a leak valve. The dosage is given in the Langmuir unit (1 Langmuir = 1.33 × 10$^{-6}$ Pa s).

The NRA measurements were performed in another UHV chamber with the $^1$H($^1$N, $\alpha$)$^4$C nuclear reaction using $^1$H$^5$N ion beams (29, 30) provided by the van de Graaff tandem accelerator at The University of Tokyo. By detecting the 4.43-MeV $\gamma$-ray emitted by the reaction, the hydrogen concentration can be measured. This nuclear reaction has a resonance at an energy of 6.385 MeV with a narrow width of 1.8 keV. When $^1$H$^5$N ions with the resonance energy are incident on the sample, they react with only surface H atoms. When $^1$H$^5$N ions with an energy higher than the resonance energy are incident on the sample, on the other hand, the ions lose a part of their energy in the bulk and then they react with H atoms at the depth where the $^1$H$^5$N energy has reduced to 6.385 MeV. Thus, by counting the number of the emitted $\gamma$-ray as a function of the $^1$H$^5$N beam energy, one can measure hydrogen depth profiles. The absolute hydrogen concentration can be obtained by comparing with an NRA depth profile for a standard polystyrene sample (31). The ion beam current was about 15 nA in the 2 × 2 mm$^2$-beam spot on the sample.

The ARPES spectra were taken at 300 K in another UHV chamber by a hemispherical electron analyzer (Scienta SES-100) with an energy resolution of about 40 meV using 21.22-eV photons from a helium discharge source with a hemispherical electron analyzer (Scienta SES-100) with an energy resolution of about 40 meV using 21.22-eV photons from a helium discharge source with a beam-spot diameter of about 2 mm. For the parallel momentum scan the polar angle was changed from 0 to 24° at an interval of 2° from the normal direction.

Deposition of Au was conducted using heated tungsten coils loaded with Au wire at a sample temperature of 300 K and at rates of about 1.0 ML min$^{-1}$ in the LEED, AES, and TDS measurements, 0.9 ML min$^{-1}$ in the NRA...
measurements, and 0.015 ML min⁻¹ in the ARPES measurements. One monolayer is defined as 9.35 × 10⁻¹⁴ atoms cm⁻² for Pd(110). The amount of deposited Au atoms was monitored by a quartz oscillator placed near the sample. In the ARPES measurement, the amount of deposited Au was determined from the ARPES spectra on the basis of a previous study where the Au-derived band almost saturates at 1 ML. In the TDS experiments shown in Fig. 1, each Au layer was deposited after cleaning the sample. In the TDS experiments shown in Fig. 2, the amount of deposited Au was incrementally increased with cycles of Au deposition of 0.1 ML followed by annealing at 700 K for 5 min. In the ARPES experiment shown in Fig. 2, Au was additionally deposited after cycles of Au deposition and annealing at 700 K for 5 min. The as-grown 2.4 ML Au/Pd(110) surface in Fig. 5 was prepared by the deposition of 1.67 ML Au on the 0.73 ML Au/Pd(110) surface and this surface corresponds to a thick Au layer grown on Au/Pd(110).

Adiabatic potentials for a single H atom in the (110) surface structures were evaluated by theoretical calculations based on DFT with the generalized gradient approximation within Perdew, Burke, and Ernzerhof formalism (32). We applied the PHASE code (33). The calculations were performed using projector-augmented wave potentials (34) for hydrogen, palladium, and gold atoms with equally spaced 16 k points for Brillouin-zone samplings. The cutoff energies are 25 Ry for the wave functions and 196 Ry for the augmented electron densities. The (110) surface structures are represented by a repeated slab of a (2 × 3 × 6) unit cell with periodic boundary conditions. Inversion symmetry with respect to the slab center is implemented to increase the computational efficiency. Reaction rates can be determined by examining the activated H atoms near the saddle points on potential energy surfaces as predicted by transition-state theory. First, the surface structures including the H atom at octahedral or tetrahedral sites are relaxed according to be in equilibrium positions to find initial and final metastable states during the H-atom migration. At each point on the H migration path, the H atom is relaxed into equilibrium positions on the plane normal to the migrating direction, while the other atoms are relaxed into equilibrium positions. Thus, the H atom can be moved through the saddle points on potential energy surfaces between the octahedral and tetrahedral sites from the bulk toward the (110) surface, leading to the most plausible path for the H-atom migration.

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