Supporting Information

Near-Surface Accumulation of Hydrogen and CO Blocking Effects on a Pd-Au Alloy

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S1. AES analysis

In the AES spectra, Au NOO and Pd MNN peaks appear at 70 and 330 eV, respectively. The peak-to-peak intensity ratio I_{Au}/I_{Pd} of Au (I_{Au}) relative to Pd (I_{Pd}) is an indicator of the surface Au concentration. We estimated the surface Au concentration on the basis of the method proposed by Jabloński et al.[1] The AES intensities of I_{Au} and I_{Pd} are given by

$$I_{Au} = k_{Au} \sum_{n=1}^{\infty} x_{Au,n} \exp\left(-\frac{z_n}{\lambda_{Au} \cos\theta} \right) \qquad \text{(S1)}$$

$$I_{Pd} = k_{Pd} \sum_{n=1}^{\infty} \left(1 - x_{Au,n}\right) \exp\left(-\frac{z_n}{\lambda_{Pd} \cos\theta} \right) \qquad \text{(S2)}$$

where k_{Au} and k_{Pd} are constants including instrumental parameters and the backscattering factor for Au and Pd AES spectra, respectively, $x_{Au,n}$ is the Au concentration of the n-th layer, z_n is the distance of the n-th layer from the surface, λ_{Au} and λ_{Pd} are the escape depths of the Auger electrons for Au (70 eV) and Pd (330 eV), respectively, and θ is the acceptance angle of the analyzer. k_{Au} and k_{Pd} are assumed to be independent of the composition of the alloy. We integrated Eqs. S1 and S2 over θ from 0 to 51°, because we used an LEED optics with an acceptance angle of 51 ° as an energy analyzer. We obtained I_{Au}/I_{Pd} = 0.81 by measuring the AES spectrum from Au(1 ML)-covered Pd(110), which corresponds to $x_{Au,1}$ = 1 and $x_{Au,n>1}$ = 0. With $z_n = nd$ (d = 0.14 nm), λ_{Au} = 0.4 nm, and λ_{Pd} = 0.8 nm,[1] the ratio k_{Au}/k_{Pd} = 3.4 is obtained using Eqs. S1 and S2. With known I_{Au}/I_{Pd}, one can estimate $x_{Au,n}$ by finding $x_{Au,n}$ that reproduces the experimental I_{Au}/I_{Pd}. We assumed that $x_{Au,n}$ (n = 1) for the (1×1) surface and $x_{Au,n}$ (n = 1 and 2) for the (1×2) surface take values x_{Au} different from the bulk value of 0.3. Since the half of the top layer is missing for the (1×2) missing-row surface, we used $z_n = (n\text{-}0.5)d$ (the thickness of the top layer is half of the other layers) and reduced the contribution of the top layer in Eqs. S1 and S2 to half for the calculation of the (1×2) surface.

The inset of Fig. S1 shows the calculated I_{Au}/I_{Pd} using Eqs. S1 and S2 as a function of x_{Au}. The

surface Au concentration as a function of the annealing temperature can be estimated as shown in Fig. S1 by comparing the experimental I_{Au}/I_{Pd} in Fig. 1 in the main text. Since the LEED pattern is (1×1) below 700 K and (1×2) above 700 K (see main text), the estimated values for (1×1) and (1×2) in Fig. S1 correspond to the surface Au concentration below and above 700 K, respectively. Since the LEED pattern after annealing at 700 K shows a weak (1×2) pattern, the surface Au concentration will be in the range between the (1×1) and (1×2) data. The estimated surface Au concentration is 66-77% at 700 K and 85% at 800 K. The value at 800 K agrees with a previous study for $Pd_{70}Au_{30}(110)$[2] where the surface Au concentration is in the range 80-100% after annealing between 713 and 803 K. It should be noted that a Pd-rich layer might be present below the surface. If Pd enrichment up to 90% in the layer just below the Au-rich layers is considered, the surface Au concentration is estimated to be 74-90% at 700 K and 94% at 800 K. Thus, the Au concentration at the surface is estimated to be 66-90% at 700 K and 85-94% at 800 K depending on the Pd concentration just below the Au-rich layers. For more detailed analysis of the layer-dependent composition, AES is not sufficient but other experimental approaches are required. Our AES analysis would underestimate the surface Au concentration, because the AES data were taken around 125 K where adsorption of impurities such as CO would suppress the Au signal preferentially. The TDS and NRA results indicate that the surface Au concentration is around 90% at 700 K (see main text).

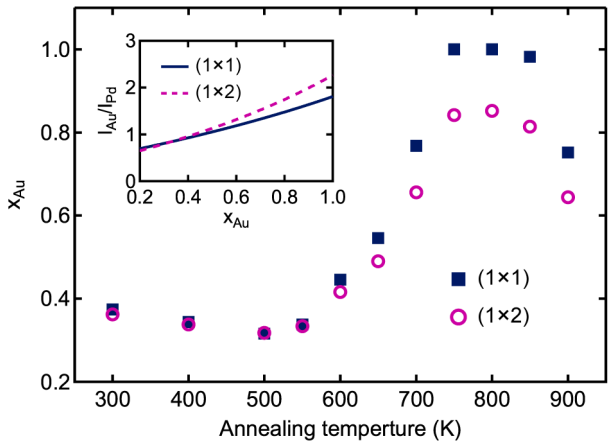

Figure S1. Estimated surface Au concentration x_{Au} as a function of annealing temperature. The inset shows calculated I_{Au}/I_{Pd} as a function of x_{Au}.

S2. Dependence of H_2 TDS on annealing temperature

Figure S2 shows the relation between the total amount of absorbed hydrogen measured by TDS and the AES intensity ratio I_{Pd}/I_{Au} as a function of the annealing temperature. Each TDS spectrum was measured after 100 L H_2 exposure at 140 K. It is clear that the amount of

hydrogen is higher as I_{Pd}/I_{Au} is higher. Our NRA measurements (Fig. 3 in the main text) showed that hydrogen is mainly absorbed into the interior of the substrate, not adsorbed on the surface. Since I_{Pd}/I_{Au} is an indicator of the surface Pd concentration, this result indicates that hydrogen is absorbed through the site related to surface Pd atoms.

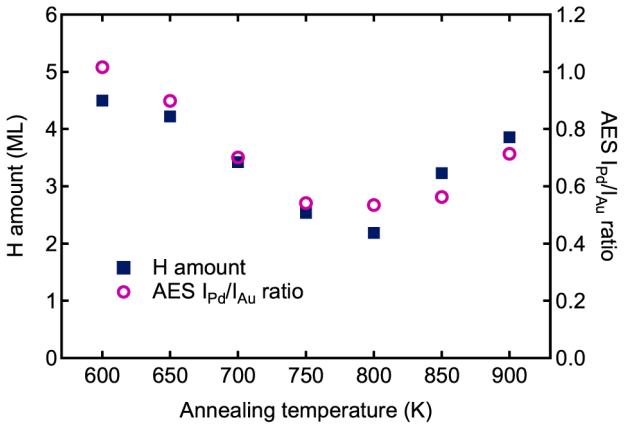

Figure S2. Amount of absorbed hydrogen measured by TDS after 100 L H_2 exposure at 140 K and AES intensity ratio I_{Pd}/I_{Au} as a function of annealing temperature.

S3. Dependence of CO TDS on annealing temperature

Figure S3 shows the CO TDS spectra from $Pd_{70}Au_{30}$(110) annealed at 700 and 800 K after 5 L CO exposure at 100 K. Five CO desorption peaks were observed at 170, 225, 300, 360, and 420 K. As the annealing temperature is raised from 700 to 800 K, the intensity at 420 K decreases while that at 170 K increases. The total CO coverage is estimated to be 0.27 ML for both annealing temperatures by comparing our TDS spectrum taken from the 1 ML CO-covered Pd(110).[3,4]

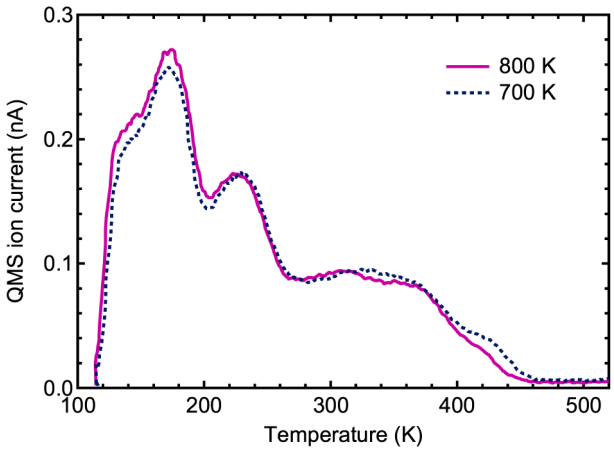

Figure S3. CO TDS spectra from $Pd_{70}Au_{30}$(110) annealed at 700 and 800 K after 5 L CO dosage at 100 K.

References

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