Moiré

Pd on Au(111)

Squeezing and Stretching Pd thin films: a High-resolution STM study of Pd/Au(111) and Pd/Cu(111) Bimetallics

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Abstract: Pd bimetallic alloys are promising catalysts, especially for heterogeneous reactions involving hydrogen, as they exhibit increased activity and reduced demand for expensive precious metals. Using scanning tunneling microscopy, we examine the structure of Pd thin films on Cu(111) and Au(111) and demonstrate compression and expansion, respectively, of the bulk Pd lattice constant in the film. The relative binding strength of H to the two surfaces, inferred via tip-induced diffusion barriers, suggests that the strain in these systems may alter adsorbate binding and corroborates well-known trends in d-band shifts calculated by density functional theory. Modification to the topography and activity of Pd films based on the choice of substrate metal illustrates the value of bimetallic systems for designing less expensive, tunable catalysts.

Keywords: metal alloys, thin films, moiré, palladium, gold, copper, hydrogen, STM

1. Introduction

Heterogeneously catalyzed reactions involving hydrogen, including hydrogenations, dehydrogenations, or hydrodesulfurizations, are vital to many modern chemical industries.^{1, 2} One of the most commonly used metal catalysts for these reactions is Pd, which has a wide range of applications in processes ranging from H separation and storage, to fuel cells.³⁻⁷ Despite the importance of Pd-catalyzed reactions, the mechanisms critical to reaction energetics through which hydrogen adsorbs on and absorbs in Pd are not completely understood. Toward this end, several studies have examined the interaction of hydrogen on Pd(111) surfaces.⁸⁻¹⁴ Mitsui et al. studied the dissociative adsorption of hydrogen on Pd(111) and demonstrated that various H overlayer structures form as a function of H surface coverage.^{8, 9} Using high-resolution scanning tunneling microscope (STM) images, they illustrated that the preferred binding site for H on Pd(111) is the fcc three-fold hollow site and at high vacuum aggregates of 3 or more Pd vacancies are required to efficiently dissociate H₂. It has also been shown that greater exposures of H₂ cause surface H atoms to migrate to subsurface Pd sites.^{10, 11} Weiss and coworkers examined the dynamics of surface and subsurface H on/in Pd(111) and showed that the diffusion of surface H is induced at 4 K with inelastic excitation by tunneling electrons.^{12, 13} They also demonstrated the ability to excite

bulk hydrogen and selectively populate subsurface sites with high spatial precision.¹³ Importantly, the presence of subsurface H in Pd(111) was found to alter the electronic and chemical properties of the metal surface.¹³ Mitsui et al. later described a similar means to manipulate surface and subsurface H on and in Pd(111) using local electric fields.¹⁴

Due to the high cost of Pd, many groups have also explored more inexpensive alternatives to pure Pd, such as bimetallic Pd alloys, ultra-thin Pd films, and single atom alloys, as that these alternatives use smaller amounts of the active element.¹⁵⁻¹⁷ Many surface and near surface Pd alloys were shown to possess higher activity and selectivity than pure Pd or the supporting metals for various film thicknesses from the millimeter-scale (e.g. Pd membranes¹⁸⁻²⁰) to the nanometer-scale (e.g. clusters and isolated Pd atoms²¹⁻²⁶). For example, Kyriakou et al. have shown that isolated Pd atoms in Cu efficiently dissociate H₂ and provide unique reactivity for hydrogenation reactions.^{23, 26, 27} These novel catalytic properties result from the differing electronic structures (ligand effects), site distribution (ensemble effects), and lattice constants (strain effects) between the Pd and support metal.^{15, 16, 23, 26, 27}

Though it can be difficult to distinguish the contributions from the various effects of alloying, density functional theory (DFT) calculations and STM experiments have shown that stretched metal film surfaces (i.e. a film of a smaller metal on top of a larger substrate) often display enhanced catalytic activity due to film strain.²⁸⁻³⁰ DFT calculations showed that expansion of a film's lattice constant causes a decrease in the overlap of *d* electrons from neighboring metal atoms and thus a decrease in the width of the film's *d*-band; in order to maintain the *d*-state occupancy, the *d*-band center of the metal film shifts toward the Fermi level. This shift leads to stronger adsorbate-surface interactions, such as greater adsorption energies and lower activation energy barriers to dissociation. For example, a recent DFT study by Pereira et al. examined the effect of expansive strain on Pd by comparing 1 monolayer (ML) of Pd on Au(111) to pure Pd(111).³¹ The calculations showed that, compared to Pd(111), the *d*-band center of surface Pd in the Pd/Au(111) system shifts 0.3 eV closer to the Fermi level and that the H adsorption energy on Pd/Au(111) is higher.

In addition to modification of electronic states, thin films exhibit unique topographic structures, such as moiré patterns and periodic dislocation networks, which relieve strain and can organize nanostructure arrays.³²⁻³⁸ Both superstructures result from a mismatch between the lattice constant of the film and the underlying metal substrate, except in unique cases where dislocation networks are determined by the interface energy.³² In the case of a moiré pattern, the mismatch manifests as a superstructure resulting from the periodic shift in adsorption site of the surface atoms. This makes thin films interesting systems to study the deviation of lattice constants from the pure metal, the effect on the *d*-band center, and how adsorption and reaction properties are altered. However, surface science experiments of the electronic and structural properties of thin films exhibiting moiré patterns are somewhat rare. Previous STM studies examined the growth and topography of Pd thin films deposited on Ni(111) and characterized the surface and interface of the system's multilayer moiré superstructure, but it was determined there

was not a change in the film's lattice constant relative to the bulk Pd spacing.^{37, 38} It is worth noting that periodic DFT studies of metal-on-metal layered systems rarely take into account any reconstructions that lead to moiré patterns and periodic dislocation networks due to the large slab size required. Therefore, it is important to examine the real surface structures and lattice spacings experimentally in order to predict how the lattice strain will affect surface binding and hence catalytic properties.

Au(111) and Cu(111) substrates, which have larger and smaller lattice constants than bulk Pd respectively, enable us to explore both compressive and expansive strain effects. Previous studies have examined the Pd/Cu(111) and Pd/Au(111) systems,³⁹⁻⁴⁴ but detailed structural models similar to those constructed for Pd/Ni(111)^{37, 38} have not been reported for either system. Our high-resolution STM images allow us to construct models for the structure of the Pd/Cu(111) and Pd/Au(111) surfaces, and we demonstrate that the Pd films' lattice constants are different compared to bulk Pd. The interaction of H with these surfaces suggests that this strain affects binding strength, consistent with the *d*-band shift trends calculated by DFT. This research provides insight into the physical and electronic structure of thin film catalytic systems and illustrates the potential value of strain effects in Pd/Au and Pd/Cu systems for the design of bimetallic catalysts.

2. Experimental Methods

All experiments were conducted using a commercially available Omicron NanoTechnology GmbH low-temperature scanning tunneling microscope operated in ultra-high vacuum (base pressure <10⁻¹¹ mbar) at 5 or 80 K. Cu(111) and Au(111) single crystals (MaTeck) were cleaned prior to experiments using a series of Ar⁺ ion sputtering (1 keV/12 μ A) and annealing (1000 K) cycles. The samples were mounted side-by-side on an STM sample plate for concurrent Pd and H₂ deposition and rapid turn-around in imaging. Pd was deposited onto the clean substrates at room temperature via physical vapor deposition using an electron beam evaporator (Focus, GmbH) in an isolated preparation chamber to produce coverages between 1 and 5 ML. The sample was then transferred to the STM chamber in < 5 min and cooled to 80 K in < 1 hour. H₂ was deposited onto the Pd films at 80 K using a high-precision leak valve in the STM chamber and produced 1 ML 1x1 H covered surfaces. Diffusion of H overlayer vacancies was induced using perturbative scanning conditions, as noted in the text. Voltage pulses were performed with the feedback-loop turned off over specific surface locations at the conditions described. The moiré pattern periodicity was found with linescans by averaging multiple periods (typically 4-6). About 20 measurements of this nature were taken for each system across several images and multiple days of experimentation, representing over 70 periods on Cu(111) and over 90 periods on Au(111). The error reported in the text represents one standard deviation from the average period.

3. Results

3.1 Structure of Pd/Cu(111) and Pd/Au(111)

STM images taken after deposition of Pd onto Cu(111) and Au(111) reveal superstructures with hexagonal symmetry in the Pd overlayers (Figure 1). These surface features can be attributed to a mismatch between the lattice constant of the Pd film ($\alpha_{\text{Pd}} = 2.75 \text{ \AA}$) and the underlying crystals ($\alpha_{\text{Cu}} = 2.56 \text{ \AA}$ or $\alpha_{\text{Au}} = 2.88 \text{ \AA}$). The moiré pattern of the Pd/Cu(111) system exhibits six-fold symmetry with 6 diffuse circular protrusions surrounding a central, pronounced protrusion with a darker outline (Figure 1 A, B). The unit cell of the moiré pattern is defined by the pronounced features, resulting in a period of $5.62 \pm 0.56 \text{ nm}$. The Pd/Au(111) system exhibits a more complex moiré pattern, which consists of bright rings that are surrounded by three dark circles separated by bright lines (Figure 1 C, D). This moiré pattern, defined here by the central bright rings, has a relatively large period of $8.70 \pm 0.78 \text{ nm}$. Our experiments examined between 1 and ~ 4 MLs of Pd and we didn't see significant changes in the moiré pattern which implies that the Pd lattice strain does not change much with layer thickness.

Figure 1. Moiré patterns of pseudomorphic Pd thin films on Cu(111) and Au(111). Coverage = 1-3 ML. Scanning temperature = 80 K. All scale bars = 10 nm. Unit cells of the superstructure and underlying crystal directions are indicated in blue. (A) and (B) Pd/Cu(111); (C) and (D) Pd/Au(111).

To determine if the unit cell period of the Pd film superstructures are consistent with the mismatch of the bulk Pd lattice constant and the lattice constants of the Cu and Au substrates, simple geometric models were constructed using the bulk lattice constants of each metal. We model the moiré pattern based off the beating phenomenon of two waves with slight differences in wavelength. Using trigonometric identities we can derive Equation 1 for the wavelength of a beating envelop, which will manifest in our samples as the moiré spacing ($a_{\text{moiré}}$) of the Pd overlayer.

$$\frac{1}{a_{\text{moiré}}} = \left| \frac{1}{a_{\text{Pd}}} - \frac{1}{a_{\text{sub}}} \right| \quad (1)$$

Subsequently, it can be shown that Equation 2 represents the propagation of uncertainty (σ) through Equation 1 when calculating the Pd atom spacing, a_{Pd} , from the measured value of the moiré pattern, $a_{moiré}$.

$$\frac{\sigma_{Pd}}{a_{Pd}} = \left(\frac{a_{Pd}}{a_{moiré}} \right) \cdot \frac{\sigma_{moiré}}{a_{moiré}} \quad (2)$$

From our measurement of the moiré period for Pd on Cu we find that the Pd atoms are spaced 0.268 ± 0.001 nm apart, which is a 2.5% compression of the Pd lattice relative to the bulk lattice constant. For the analysis of the Pd/Au interface, it is important to note that we do not consider the Au herringbone reconstruction in this model because others and we find that it is lifted upon Pd deposition.⁴³ For the Pd overlayer on Au we find that the Pd atoms are spaced 0.279 ± 0.001 nm apart, which is a 1.5% expansion of the lattice relative to the bulk Pd lattice.

Viewing these strained overlayers, it is expected that the center of the Pd *d*-band would shift away from the Fermi level in the compressed Pd/Cu system and toward the Fermi level in the expanded Pd/Au system. A corresponding change in the chemistry of the surface should follow, with compression leading to weaker adsorbate binding and expansion leading to stronger binding.^{9, 28, 29}

3.2 H Interactions with Pd/Cu(111) and Pd/Au(111)

Since hydrogen adsorbs dissociatively on Pd, the interaction of H overlayers with the two Pd film systems can serve as a probe for the chemistry of the two surfaces. After saturating the surfaces with H, a small number of persistent vacancies in the resulting H overlayer is unavoidable, regardless of H₂ exposure due to the mechanism of H₂ dissociation on Pd(111)-type surfaces that requires at least 3 adjacent binding sites to be unoccupied.⁸ These vacancies in the H overlayer appear as bright protrusions because H atoms on metals appear as depressions. These vacancies order in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ packing structure if enough energy is available for the vacancies to laterally diffuse and coalesce.¹³ It is worth noting that ordered patches of vacancies are not H-free areas, but consist of the lower density 2H- $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase surrounded by the majority H-(1 $\times$ 1) phase.¹³

To probe the relative H adsorption strength in the two systems, the scanning voltage was increased incrementally to find the minimum voltage needed to induce lateral motion of the H atoms (Figure 2). For Pd/Cu(111), vacancies began to move, disappear, or appear streaky when the scanning voltage was raised above 300 mV. The low sample temperature quenches all thermally induced diffusion and ensures that the H diffusion is induced by the STM tip. For the Pd/Au(111) system, raising the voltage to 300 mV was insufficient to induce diffusion, and movements were not observed on Pd/Au(111) until a 500 mV or greater scanning bias was used. For both systems, equivalent results were produced using negative voltages. The higher barrier to tip-induced lateral H diffusion on Pd/Au(111) versus Pd/Cu(111) suggests the expanded Pd surface in the Pd/Au system binds the H more tightly, consistent with the energetic description

provided by *d*-band calculations. This argument is based on the linear relationship between the diffusion barrier and the binding energy of a species which leads to stronger bound adsorbates having higher diffusion barriers.

Figure 2. STM tip induced H overlayer diffusion on Pd thin films. All scale bars = 2 nm. (A) and (B) Pd/Cu(111). At a scanning bias of 300 mV, movement was induced as evident by the streaking and diffusion of H vacancies (i.e. H diffusion). (C) and (D) Pd/Au(111). STM images taken at nonperturbative scanning conditions before and after a perturbative scan at 500 mV. Blue arrows and circles highlight diffusion events between images.

To demonstrate the precision with which the local density of H on Pd thin film systems can be controlled by STM, additional experiments were carried out on Pd/Cu(111) in which the diffusion of H vacancies was directed into small ordered patches on the surface over the time-frame of 24 consecutive STM images (Figure 3). Delivering a voltage pulse near an existing vacancy moved the vacancy towards the location of the pulse (i.e. the hydrogen diffused away from the site of the pulse). The total number of vacancies across the images is approximately conserved, indicating that the voltages used are not energetic enough to desorb H and are simply rearranging the H overlayer. This exercise demonstrates reversible fine control over the local density of surface H on thin film Pd systems.

Figure 3. STM images demonstrating the tip-directed diffusion of H. Scanning temperature = 5 K. All scale bars = 2 nm. STM images are excerpts from the 24-image series in which H vacancies were controllably directed into an ordered island.

4. Conclusion

By carefully measuring moiré patterns, creating simple structural models, and examining a probe molecule's interaction with the surface, we have elucidated the structure of the Pd/Cu(111) and Pd/Au(111) layer on layer systems. The observed contraction of the Pd lattice on Cu and expansion of the Pd lattice on Au indicates that strain in thin film bimetallic alloys can be intentionally tuned via the lattice constant of the supporting metal. Our results for these systems support DFT calculated trends of *d*-band shifts which suggests that tuning the lattice constant of a metallic film via a choice in substrate metal can be a useful way to control the reactivity of the alloy's surface. These insights, obtained using surface science techniques, provide an important foundation for the directed design of better bimetallic thin film or nanoparticle catalysts. Furthermore, compared to Pd(111) single crystals which, even after months of UHV cleaning still contain defects and impurities, these films offer a simple, high purity system with which to study Pd surface chemistry.

ACKNOWLEDGEMENTS

We thank the Division of Chemical Sciences, Office of Basic Energy Sciences, Condensed Phase and Interfacial Molecular Science Program, U.S. Department of Energy under Grant No. FG02-10ER16170 for support of this work.

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