Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Squeezing and stretching Pd thin films: A high-resolution STM study of Pd/Au(111) and Pd/Cu(111) bimetallics

Mishan E. Blecher, Emily A. Lewis, Alex Pronschinske, Colin J. Murphy, Michael F.G. Mattera, Melissa L. Liriano, E. Charles H. Sykes *

Department of Chemistry, Tufts University, Medford, MA 02155, USA

ARTICLE INFO

Available online xxxx

Keywords:
Metal alloys
Thin films
Moiré
Palladium
Gold
Copper
Hydrogen
STM

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 the 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.

© 2015 Elsevier B.V. All rights reserved.

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 H_2. It has also been shown that greater exposures of H_2 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 membranes [18–20]) to the nanometer-scale (e.g. clusters and isolated Pd atoms [21–26]). For example, Kyriakou et al. have shown that isolated Pd atoms in Cu efficiently dissociate H_2 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

* Corresponding author.

http://dx.doi.org/10.1016/j.susc.2015.06.015
0039-6028/© 2015 Elsevier B.V. All rights reserved.

Please cite this article as: M.E. Blecher, et al., Squeezing and stretching Pd thin films: A high-resolution STM study of Pd/Au(111) and Pd/Cu(111) bimetallics, Surf. Sci. (2015), http://dx.doi.org/10.1016/j.susc.2015.06.015

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 the adsorption site of the surface atoms. This makes thin films interesting systems in studying the deviation of lattice constants from 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 that 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 the 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 the experiments were conducted using a commercially available Omicron NanoTechnology GmbH low-temperature scanning tunneling microscope operated in an 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 the experiments using a series of Ar + ion sputtering (1 keV/12 μA) and annealing (1000 K) cycles. The samples were mounted side-by-side on an STM sample plate for concurrent Pd and H_2 deposition and rapid turn-around in imaging. The Pd was deposited onto 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 h. H_2 was deposited onto the Pd films at 80 K using a high-precision leak valve in the STM chamber and produced 1 ML 1 × 1 H covered surfaces. The 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 the deposition of Pd onto Cu(111) and Au(111) reveal superstructures with hexagonal symmetry in the Pd overlayers (Fig. 1). These surface features can be attributed to a mismatch between the lattice constant of the Pd film ($\alpha Pd = 2.75$ Å) and the underlying crystals ($\alpha Cu = 2.56$ Å or $\alpha Au = 2.88$ Å). 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 (Fig. 1 A, B). The unit cell of the moiré pattern is defined by the pronounced features, resulting in a period of 5.62 ± 0.56 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 (Fig. 1 C, D). This moiré pattern, defined here by the central bright rings, has a relatively large period of 8.70 ± 0.78 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.

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 on the beating phenomenon of two waves with slight differences in wavelength. Using trigonometric identities we can derive Eq. (1) for the wavelength of a beating envelop, which will manifest in our samples as the moiré spacing ($a_{moiré}$) of the Pd overlayer.

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

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

$$\frac{\sigma_{Pd}}{a_{Pd}} = \frac{a_{Pd}}{a_{\text{moiré}}} \cdot \frac{\sigma_{\text{moiré}}}{a_{\text{moiré}}} \tag{2}$$

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 H_2 exposure due to the mechanism of H_2 dissociation on Pd(111)-type surfaces that requires at least 3 adjacent

Please cite this article as: M.E. Blecher, et al., Squeezing and stretching Pd thin films: A high-resolution STM study of Pd/Au(111) and Pd/Cu(111) bimetallics, Surf. Sci. (2015), http://dx.doi.org/10.1016/j.susc.2015.06.015

Download English Version:

https://daneshyari.com/en/article/5421462

Download Persian Version:

https://daneshyari.com/article/5421462

Daneshyari.com