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Growth of epitaxial thin Pd(1 1 1) films on Pt(1 1 1) and oxygen-terminated FeO(1 1 1) surfaces

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Abstract

Thin Pd films (1–10 monolayers, ML) were deposited at 35 K on a Pt(1 1 1) single crystal and on an oxygen-terminated FeO(1 1 1) monolayer supported on Pt(1 1 1). Low energy electron diffraction, Auger electron spectroscopy, and Kr and CO temperature programmed desorption techniques were used to investigate the annealing induced changes in the film surface morphology. For growth on Pt(1 1 1), the films order upon annealing to 500 K and form epitaxial Pd(1 1 1). Further annealing above 900 K results in Pd diffusion into the Pt(1 1 1) bulk and Pt–Pd alloy formation. Chemisorption of CO shows that even the first ordered monolayer of Pd on Pt(1 1 1) has adsorption properties identical to bulk Pd(1 1 1). Similar experiments conducted on FeO(1 1 1) indicate that 500 K annealing of a 10 ML thick Pd deposit also yields ordered Pd(1 1 1). In contrast, annealing of 1 and 3 ML thick Pd films did not result in formation of continuous Pd(1 1 1). We speculate that for these thinner films Pd diffuses underneath the FeO(1 1 1).

Keywords: Auger electron spectroscopy; Thermal desorption spectroscopy; Epitaxy; Growth; Surface structure, morphology, roughness, and topography; Palladium; Platinum; Iron oxide; Carbon monoxide; Metallic films

1. Introduction

Tailoring of the electronic and chemical properties of metals by nanoscaling has proven to be an extremely powerful approach in material design [1–9]. Palladium with its prominent catalytic and electrochemical properties serves as a prime example. Thin Pd films as well as supported Pd nanoparticles have been studied on a number of metal and metal–oxide supports [1–6]. It has been shown that in the case of metal supported Pd, the electronic properties change dramatically with the empty state density in the valence band of supporting metal [10]. This charge transfer can be directly observed in the increased core level and valence-band binding energies determined from photoemission experiments. Chemically, this charge transfer results in a dramatic decrease in the CO adsorption energy which has been shown to correlate directly with the shift in electronic levels [1,4,10–13]. A subsequent theoretical study by Nørskov et al. has explained the relationship between the core level shifts and CO chemisorption by correlating the energy of the center of the metal d band and the magnitude of the overlap with the CO 5σ and $2\pi^*$ states [4].

In the case of Pd deposited on a Pt substrate, significant electronic effects are not expected since both atoms have the same number of valence electrons. The interest in using Pt(1 1 1) as a support is mostly related to the ability to preserve the chemical properties of Pd while eliminating its ability to absorb H_2 in the bulk. This approach has been primarily explored in a number of electrochemical studies of Pd monolayer-modified Pt electrodes [5,14–16].

In related ultrahigh vacuum (UHV) studies, the initial stages of Pd growth on Pt(1 1 1) were explored using X-ray, ultraviolet photoelectron, and Auger electron spectroscopies (XPS, UPS, and AES) [17,18]. A key finding of these studies is the observation of layer-by-layer (Frank-van der

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Merwe) growth upon room temperature deposition. Contrary to previous studies we have carried out Pd deposition (1–10 ML) at very low temperatures (~35 K) under conditions of limited surface mobility [19] and studied the thermally induced ordering of such films. Additionally, we have also explored the adsorption properties of such films as a function of their thickness. In our ongoing studies (to be published separately), thin epitaxial Pd films are employed to understand the roles surface and bulk atomic hydrogen play in heterogeneous chemical reactions employing Pd as a catalyst.

Nucleation of Pd particles on oxides, their deposition temperature dependent size distribution, and ultimately their catalytic activity has been explored in numerous surface science studies [1–3,9]. In marked contrast to the layer-by-layer growth observed on metal substrates, Pd deposition on most oxide surfaces leads to formation of three-dimensional clusters via a mechanism commonly termed Volmer–Weber growth [2,3,9]. Recent studies have shown that flat, epitaxial Pd films [20,21] can be grown on oxygen-terminated FeO(1 1 1) thin films (1–2 monolayer thick) deposited on Pt(1 1 1). The observed metal wetting was initially thought to be due to the high surface energy associated with the polar nature of the oxygen-terminated FeO(1 1 1) surface [20]. The first scanning tunneling microscopy (STM) studies of Pd deposition on FeO(1 1 1) concluded that the Pd films wet the FeO(1 1 1) surface up to temperatures as high as 600 K [20,21]. A very recent follow up study [22] employing CO adsorption, infrared reflection adsorption spectroscopy (IRAS), photoelectron spectroscopy (PES), and STM demonstrated that the behavior of Pd on the FeO(1 1 1) is more complex. It was shown that at high temperatures (>600 K) Pd dewets from the FeO(1 1 1) surface due to diffusion underneath the FeO(1 1 1) film [22].

In this study we use low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and temperature programmed desorption (TPD) of Kr and CO to determine the Pd film morphology and its adsorption properties upon deposition under conditions of limited surface mobility [19] at 35 K and after subsequent thermal annealing up to 1300 K. Both Pt(1 1 1) and oxygen-terminated FeO(1 1 1) supported on Pt(1 1 1) are employed as substrates. We show that 1–10 monolayer (ML) thick Pd films deposited on Pt(1 1 1) are initially disordered but order upon heating to 500 K, forming flat, epitaxial Pd(1 1 1). The physisorption of Kr and chemisorption of CO on Pd films of various thickness (1–10 ML) are explored. We show that even 1 ML thick Pd films annealed to 600 K have structural and chemical properties virtually identical with those of a bulk Pd(1 1 1) single crystal as evidenced by LEED and Kr and CO desorption. Further, we have determined that the thermal stability of the Pd films is not determined by Pd desorption but rather by diffusion into and alloying with the underlying Pt(1 1 1) substrate around 900 K. The Pd overlayers on FeO(1 1 1) behave very different. Only the 10 ML thick Pd film ordered upon annealing to 500 K. Thinner films dewet from the FeO(1 1 1) surface before the formation of ordered Pd(1 1 1). Annealing above 500 K leads to dewetting of the 1–10 ML thick films and Pd diffusion underneath the FeO(1 1 1) in agreement with previous studies [20–22].

2. Experimental

The experiments were conducted in an UHV chamber with a base pressure of $\sim 1 \times 10^{-10}$ Torr. The Pt(1 1 1) substrate (disk, 10 mm in diameter, 1 mm thick) was cleaned using standard procedures including a sequence of neon-ion bombardment at 30 K, O_2 annealing at 1200 K (5 min, 2×10^{-7} Torr), and annealing in UHV at 1300 K. The temperature of the Pt(1 1 1) substrate was measured using a chromel–alumel (type K) thermocouple spot welded to the edge of the sample and could be controlled from 20 to 1300 K. An absolute temperature calibration was performed using the multilayer desorption of various gases (N_2, Ar, O_2 and H_2O) from the sample surface [23]. The resulting uncertainty in the absolute temperature is estimated to be ±2 K.

The surface composition and purity was measured using cylindrical mirror analyzer AES (PHI, 10-155A). Surface order was determined using LEED (Princeton Research, RVL 8-120). Both instruments were warmed up (filament on) overnight prior to each experiment and kept on during the entire experimental run (typically a full day) to ensure the stability and reproducibility of the signal. The AES spectrum from initially clean Pt(1 1 1) at the beginning of each experimental run was compared with that from 1300 K annealed Pt(1 1 1) at the end of the film-annealing sequence to confirm that the signals remained constant throughout the entire experiment. Despite numerous sputter-anneal cycles, small residual amounts of Fe and Pd (<2%, sensitivity corrected) [24] were observed on the surface by AES. Our studies using Kr and CO temperature programmed desorption (TPD) (see below) suggest that this small amount of contamination does not effect the adsorption properties of the Pt(1 1 1) single crystal.

Thin FeO(1 1 1) films (~1 FeO bilayer thick) were grown epitaxially on the Pt(1 1 1) substrate using a previously published procedure [25–28]. The iron was evaporated onto the Pt(1 1 1) substrate using a high temperature effusion-cell (CreaTec). To grow a film, one monolayer of Fe was deposited on the Pt(1 1 1) surface at 300 K, and then oxidized at 870 K in an O_2 atmosphere (3 min, 10^{-6} Torr). An additional cycle of Fe deposition and O_2 oxidation at 1000 K (3 min, 1×10^{-6} Torr) was employed to obtain the final FeO(1 1 1) film. This process proved to be highly reproducible and yielded high quality FeO(1 1 1) films. The AES spectrum from the FeO was identical with that previously published for one bilayer thick FeO(1 1 1) [26]. It is dominated by O_{KLL} at 510 eV and Fe_{LMM} at 600, 654, and 705 eV. Additionally, all Pt_{NOO} related features, albeit reduced in intensity to ~60% of their value on clean Pt(1 1 1) surface are also present. We were unable to further