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Effects of substrate shape, curvature and roughness on thin heteroepitaxial films of Pt on Au(1 1 1)

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ABSTRACT

The growth of thin (1–10 nm) films of Pt on Au(1 1 1) was studied in order to understand and clarify differences in growth mode observed in ultra-high vacuum (UHV) studies and in electrochemical deposition studies. It was found that on flat Au(1 1 1), Pt grows in a layer-by-layer growth mode, but if the gold substrate is exposed to an acidic environment prior to Pt deposition, then the substrate becomes nanoscopically rough (islanded) and Pt growth follows a pseudo-Stranski–Krastanov (SK) growth mode in which an initially thin wetting layer becomes rougher with increasing film thickness. An analysis of curvature effects on epitaxial growth mode shows that thermodynamic curvature effects involving surface stress are negligible for the Pt/Au(1 1 1) system. Rather, the apparent SK growth is linked to kinetic effects associated with inhomogeneous in-plane elastic relaxation of Pt films on rough surfaces that drive Pt atoms from pits to the tops of islands in the early stages of growth. Implications for the control of epitaxial film roughness are discussed.

1. Introduction

1.1. Motivation for studying platinum heteroepitaxy on gold

Within the heterogeneous catalysis community, significant attention is being paid to core-shell nanostructured materials, in which the properties of a thin (1–5 nm) shell are modified by electronic or mechanical interaction with a thicker core [1–3]. Much of this attention is being driven by theoretical predictions. For example, in the development of carbon oxygen reduction catalysts for fuel cells, theoretical predictions and experiments have suggested that a monolayer of Pt on Pd(1 1 1) is superior as a catalyst for this chemical reaction than Pt alone [4], the current material of choice. As a result of these and similar studies, a large effort is being made to fabricate both core-shell nanoparticles possessing industrially useful high surface areas, as well as model ultra-thin epitaxial films on substrates [5]. Comparisons between the nanoparticulate materials, thin films, and theoretical models are quite challenging. They are complicated by the polyfaceted nature of nanoparticles, thermodynamic curvature effects, and also by differences between the (electro)chemical environments and/or the ultra-high vacuum (UHV) environments that are chosen for their manufacture. In this paper, we describe a study of 1–10 nm thick epitaxial films of Pt on smooth and chemically roughened planar Au(1 1 1).

The motivation for this work comes from an observation made while making Pt-plated nanoporous gold (Pt-NPG) [6,7]. NPG is a bicontinuous mesoporous metal containing open porosity fabricated by chemical dealloying of silver from silver/gold alloys, typically in nitric acid [8]. The structure that remains after dealloying $Au_{35}Ag_{65}$, for example, is an open porous metal, nearly pure gold in composition, possessing high surface area ($\sim$5 m^2/g) with pores and ligaments each approximately 15 nm in diameter. As grains sizes in the alloy are typically >10 microns wide, the pore size of NPG is significantly smaller than the grain size, and thus when considering its microscopic properties and morphology, NPG can be considered an extended porous single crystal. For electrochemical applications, NPG is useful because it contains the high surface area of nanoparticles, but in an interconnected, mechanically robust network in which every point on the surface is electrically accessible. NPG can be made into a core-shell catalytic material by electrolessly reducing Pt onto its surface, creating thin films $\sim$1–5 nm in thickness, using methods described in Refs. [6,7]. Micrographs of the morphology of Pt-NPG are also found in these references. Briefly summarizing those results, we found that 1 nm (average)-thick films appeared conformal and smooth, but the 5 nm (average)-thick films appeared “bumpy”, consisting of islands 3–4 nm in diameter and few nanometers high. In both cases, however, the films were epitaxial, as indicated by the obvious lattice fringes in high resolution transmission electron microscope (TEM) micrographs, as well as sharp electron diffraction patterns.

In Ref. [7], it was hypothesized that the observed growth of Pt on NPG was a manifestation of Stranski–Krastanov (SK) growth

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of Pt on highly curved substrates. However, there is no report of SK growth in the literature on Pt/Au for films greater than one monolayer (ML) thick (a literature review is provided in Section 1.2). The base-level gross morphological difference between NPG and planar gold is the curvature of the substrate, of order 0.1 nm^{-1} in NPG and zero for planar substrates, and it was thought that the high curvature of the ligaments of NPG changed the surface stress and the lattice mismatch conditions, leading to SK growth. Surface stress effects on NPG are of current interest, especially as they influence actuation in electrochemical environments and the mechanical properties of NPG [9]. However, changes in substrate lattice parameter with curvature due to surface stress turn out not to be large enough to affect Pt growth on NPG, as we show in Appendix 1.

A second hypothesis regarding the growth of Pt on NPG was that approximating nanoporous gold as a smoothly curved surface was not a good approximation to the real morphology, and that a better structural model (suggested by simulation [10] but not observed, as yet, by any microscopy) was that the surface of NPG is covered with small facets just a few nanometers wide. Because growth in this picture is not occurring on infinitely wide substrates as it would for planar deposition, perhaps the elastic boundary conditions for injections of misfit dislocations and pseudomorphic growth are different from the assumption in the usual Matthews–Blakeslee model [11]. Growth on small facets might allow in-plane relaxation, perhaps preferentially driving SK growth over pseudomorphic growth. To test this hypothesis, we developed highly oriented (111) single crystals of NPG that exhibited "mesa-like" porosity, i.e., a flat topped surface with a variety of terrace widths. If the growth mode were affected by finite terrace widths, then the film morphology on the narrower terraces should be bumpy, exhibiting SK growth, while growth of the wider terraces should be layer-by-layer and remain planar. The sample preparation and microscopy of this study are interesting and will be reported elsewhere, but the results of this study were negative – planar growth was seen over all accessible terrace widths from ~50 nm to ~500 nm.

These observations combine to suggest that there was something special about surface of gold in the chemical environment in which we made Pt-NPG, and the bulk of this paper concerns this issue. Ultimately, our conclusions are that chemically induced surface roughness on Au forms during dealloying in acid and does not anneal away quickly upon taking the sample out of the electrochemical environment; rather, surfaces of gold exposed to acid are rough, specifically consisting of nanoscopic islands that template the apparent SK growth of Pt on Au. We find that this effect can be mimicked in the UHV environment, and may be useful to make films with controlled roughness on the nanometer length-scale. The primary purpose of this paper is to describe this thin film work, but our results are also applicable to growth on porous metals. In hindsight, perhaps these observations are not surprising – the observation of surface roughness induced on gold due to adsorbates (especially water) has been seen before [12]. Our contribution is to extend an examination of this effect to subsequent thin film growth.

1.2. Pt/Au growth: literature review

The earliest report on Pt/Au growth we have found is by Matthews and Jesser from 1967 [13]. They grew Pt thin films on Au surfaces of various low-index orientations in UHV including (001) and (111) using molecular beam epitaxy (MBE) and used *ex-situ* TEM to study the films after dissolving away soluble substrates on which gold substrate films were initially grown. Growth at 40 °C and 300 °C yielded identical results for all orientations – no 3D nuclei were formed at any stage of growth, the Pt films remained planar with misfit dislocations appearing at a critical thickness of ~1 nm, and the spacing between misfit dislocations was ~25 nm. They concluded, therefore, that Pt/Au growth occurred in the Frank-van-der–Merwe (FM) mode. In contrast, Sachtler et al. in 1981 [14] examined MBE growth of Pt on Au(100) using *in-situ* LEED and AES. Noting that the Auger signal during growth varies uniquely for each growth mode, they concluded that their results for the Auger signal intensity change during Pt/Au(100) growth at temperatures between 150 °C and 200 °C were best fitted by a Volmer–Weber growth mode. Sugawara and Nittono in 1991 [15] found, in agreement with Matthews and Jesser and at variance with Sachtler et al., that growth occurred in the FM mode. Their experimental regime was similar to Ref. [13] except that Pt deposition was conducted by ion-beam sputtering rather than evaporation. They imaged Pt/Au bilayers in TEM and found misfit dislocations when the Pt film thickness exceeded 1 nm.

In 1997, Uosaki and coworkers [16] electrochemically deposited Pt thin films on Au(111) surfaces at room temperature using electrolytes containing the $[PtCl_6]^{2-}$ complex. They characterized morphological evolution using *in-situ* STM and presented clear evidence of layer-by-layer FM growth albeit with some increase in surface roughness. On the other hand, Waibel et al. [17] performed a very similar study in 2002 using both $[PtCl_4]^{2-}$ and $[PtCl_6]^{2-}$ containing electrolytes, and instead found evidence for VW growth. Support for VW growth of Pt/Au was also presented by Chang and Carter [18] using simulation methods. However, another simulation study of this system by Haftel et al. [19] predicted a fairly complex evolution of the Pt film which may be best described as roughened FM growth.

Finally, in another experimental work in 1999 Pedersen and coworkers [20] studied, using *in-situ* STM, the very initial growth (up to 2.5 ML) of Pt grown with MBE in UHV on Au(111) at 100 °C. They observed marginal surface alloying that was limited to the first monolayer; subsequent monolayers grew as pure Pt with a flat morphology conformal to the substrate, without nucleation of islands. It can be concluded from their work that growth occurred in the FM mode.

This literature review is summarized in Table 1.

2. Experimental

Flat Au(111) surfaces were prepared by growing thick gold films (200–400 nm) on mica, using standard procedures [21–23]. Muscovite mica discs (Muscovite Mica Grade V-1, SPI Supplies, Westchester, PA), freshly cleaved in air, were placed in a UHV chamber with base pressure 1×10^{-10} Torr. After a few hours of pre-annealing the mica at 500 °C, Au (99.99%, Sigma-Aldrich) was deposited at ~2 nm/min from an effusion cell at 1600 °C. Post-deposition, the Au/mica discs were annealed (in UHV) at 300 °C for 4 h. The flat Au surfaces obtained were roughened by exposure to concentrated nitric acid by removing the annealed Au/mica samples and immersing them in concentrated nitric acid (70%, Sigma-Aldrich) for 1 h. The samples were then rinsed thoroughly in ultraclean running water (Millipore Milli-Q, 18.2 MΩ, 2 ppb total organic content (TOC)) multiple times, alternately in long periods of immersion and under a direct water stream. Care was taken that the acid did not de-wet the Au surface during transfer from nitric acid to water, eliminating the possibility of surface residue left behind by a receding contact line. After rinsing, the samples were covered and dried in air. In an effort to fully characterize the resulting surface, the nitric-exposed Au samples were imaged in an atomic force microscope (AFM), and examined in X-ray photoelectron spectroscopy (XPS) to study surface composition with particular interest in detecting any surface impurities and adsorbates.