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Preparation and characterization of atomically flat and ordered silica films on a Pd(100) surface

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Abstract

Ultrathin silica films with different thicknesses have been grown on a Pd(100) surface by depositing silicon in the presence of O_2. The film composition and electronic properties were characterized by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and high-resolution electron energy loss spectroscopy (HREELS). Scanning tunneling microscopy was applied to investigate the film morphology and lattice structure. The results show that the obtained films are atomically flat and highly ordered in a long range. UPS and HREELS measurements indicate that the silica film has the same electronic and vibrational properties as bulk silica. A 2.8 nm thick film exhibits low defects in the film and high thermal stability up to 800 K, as evidenced by ion scattering spectroscopy and XPS.

Keywords: Silica films; Metal-oxide interfaces; X-ray photoelectron spectroscopy; Ultraviolet photoelectron spectroscopy; High-resolution electron energy loss spectroscopy; Scanning tunneling microscopy

1. Introduction

Silicon dioxide (SiO_2) is extensively used as a catalyst support. For surface scientists it is highly desirable to develop model catalysts consisting of metal clusters or nanoparticles supported on the surfaces of SiO_2. However, the insulating properties of bulk silica cause many experimental difficulties, such as surface charging, sample mounting, sample heating and cooling.

In order to circumvent these difficulties and to explore microprocesses on a silica surface (such as nanoparticle growth, surface chemical reaction, and thus induced structure change, etc. [1–6]) using surface analysis techniques, several methods have been recently developed to synthesize ultrathin SiO_2 films, among which two methods are frequently used. One is to directly expose single crystal silicon surfaces to oxygen, as in the case of Si(111)-7×7 [1–3] and Si(100) [4,5]; the other is to deposit silicon in an oxygen atmosphere or to oxidize a silicon layer on a metal substrate, such as Mo(110) [6–8], Mo(100) [9], Mo(112) [10–14], and Ni(111) [15]. Numerous studies have been performed on the preparation and characterization of thin SiO_2 films; while a few works are on the growth of ordered SiO_2 films. Freund's group and Goodman's group have prepared monolayer crystalline silica films on Mo(112) surfaces. The typical recipe for the growth of SiO_2 on Mo(112) consisted of repeated cycles of depositing one-half monolayer of silicon onto a Mo(112) surface at room temperature (RT) followed by oxidation at 800 K. The resulting SiO_2 films were subsequently annealed in four steps, which took 15 min each in an O_2 background of 1×10^{-3} Pa with the temperature ranging from 1100 to 1250 K [12,13]. Kundu and Murata reported growth of a 4.0 nm thick crystalline SiO_2 film on a Ni(111) surface [15]. Si was deposited on a clean Ni(111) surface at RT with 3 nm thickness followed by oxidation in the presence of atomic hydrogen for 1 h at a substrate temperature of 620 K. Finally the sample was annealed at 1100 K in an ambient O_2 atmosphere of 2.6×10^{-5} Pa for 10 min.

In this paper, we report a system for easily growing atomically flat and well-ordered silica films. In our growing system, Pd(100) was chosen as a substrate, and silica films were

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grown by depositing silicon onto Pd(100) in the presence of O_2. The morphologies, electronic properties, and thermal stabilities of films have been investigated by scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), high-resolution electron energy loss spectroscopy (HREELS), and ion scattering spectroscopy (ISS).

2. Experimental details

The experiments were carried out in an Omicron multiprobe surface analysis system with a base pressure of below 3.0×10^{-8} Pa. The system consists of three ultrahigh vacuum chambers: preparation, spectroscopic and microscopic chambers. The preparation chamber is equipped with a silicon evaporator and an ion-sputtering gun for sample cleaning. The spectroscopic chamber is installed with XPS, UPS, ISS, and HREELS (LK-ELS5000). The microscopic chamber is equipped with STM (Omicron Variable-Temperature STM). The three chambers are connected with a transfer chamber, through which the sample can be transferred among these chambers by magnetically coupled probes without breaking the vacuum.

A Pd(100) single crystal was mounted on an Omicron sample plate and can be resistively heated by a pyrolytic boron nitride heater. A chromel–alumel thermocouple was spot-welded on the back side of the Pd crystal to monitor the substrate temperature. The Pd(100) sample was cleaned by repeated Ar^+ sputtering, annealing, and oxidation treatment (in $\sim10^{-4}$ Pa O_2 at >700 K) in the preparation chamber until no contaminants were detected by UPS and XPS [16, 17]. The silicon evaporator was made of a silicon strip ($\sim1\times3\times10$ mm^3), which was cut off from a high purity silicon wafer and heated by running current through the strip. Silicon dioxide is formed on the substrate at 500 K when silicon is evaporated in a 1×10^{-3} Pa O_2 background atmosphere. After the deposition of the silica films, the heating power was turned off and the oxygen pressure was still maintained for another 5 min.

The XPS data were acquired with Mg Kα ($h\nu=1253.6$ eV) radiation and the spectra were calibrated with the Pd $3d_{5/2}$ peak at 335.1 eV [18]. The pass energy of the spectrometer was 30 eV, and the Pd $3d_{5/2}$ peak exhibited a full width at half maximum (FWHM) of 1.4 eV. All UP spectra were recorded at normal emission and the photoelectron peak positions were measured with respect to the Pd(100) Fermi level (E_F). ISS spectra were collected with an incident He^+ beam energy of 1000 eV. The energy resolutions of the HREELS measurements were between 40 and 64 cm^{-1} (5–8 meV). The monochromatized electrons were incident at an angle of 55° with respect to the surface normal of the sample. The analyzer could be rotated about its axis for in- and/or off-specular measurements. The

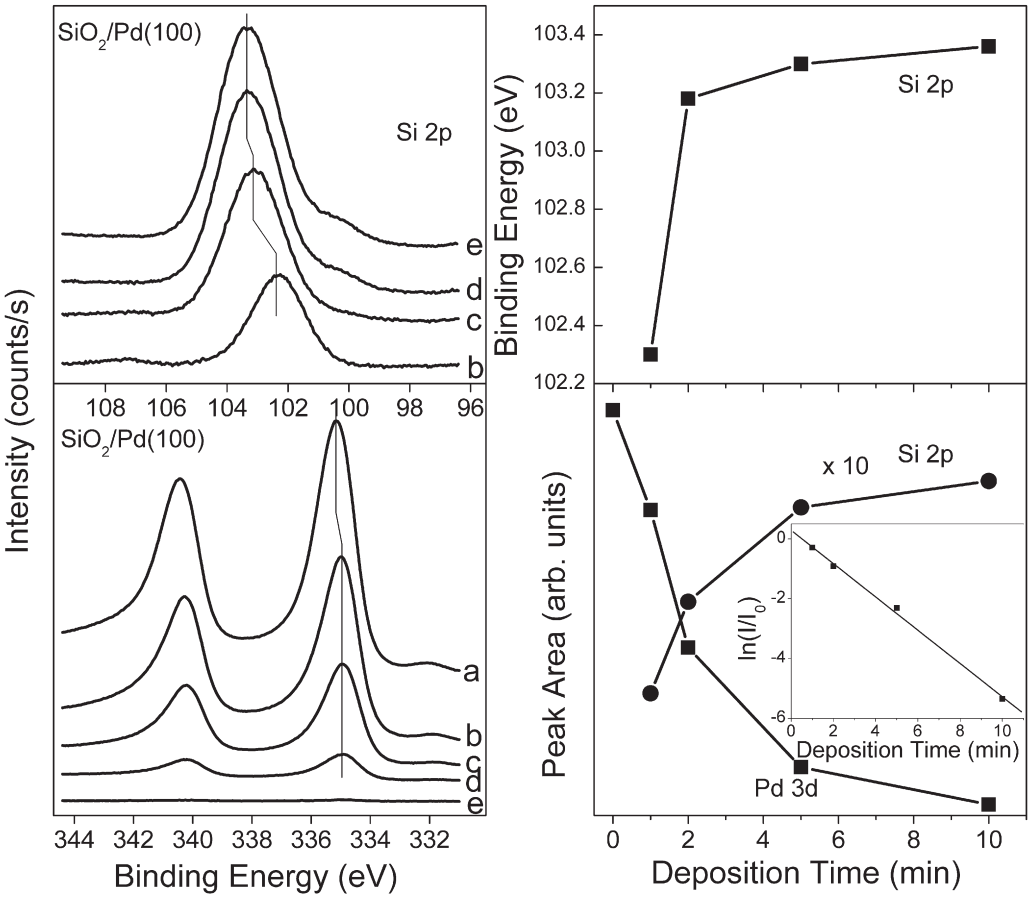

Fig. 1. Left: Si 2p and Pd 3d XP spectra of silica films on a Pd(100) surface with different thicknesses: (a) bare Pd(100), (b) 0.4 nm, (c) 1.1 nm, (d) 2.8 nm, (e) 6.5 nm; Right: (Upper) Si 2p binding energy as a function of deposition time; (Lower) Pd 3d and Si 2p peak areas as a function of deposition time; (Lower inset) Semi-logarithmic plot of the Pd 3d (signal normalized to the bare Pd(100) without SiO_2 deposition) versus deposition time.