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Effect of oxygen on the stability of Ag islands on Si(111)-7 × 7

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ABSTRACT

We have used scanning tunneling microscopy to probe the effect of oxygen exposure on an ensemble of Ag islands separated by a Ag wetting layer on Si(111)-7×7. Starting from a distribution dominated by islands that are 1 layer high (measured with respect to the wetting layer), coarsening in ultrahigh vacuum at room temperature leads to growth of 2-layer islands at the expense of 1-layer islands, which is expected. If the sample is exposed to oxygen, 3-layer islands are favored, which is unexpected. There is no evidence for oxygen adsorption on top of Ag islands, but there is clear evidence for adsorption in the wetting layer. Several possible explanations are considered.

1. Introduction

Nanoparticles of silver are technologically important for many reasons. They are used as sensors and tags because of the surface-enhanced Raman effect [1,2]. Silver is the best-known catalyst for production of ethylene oxide from oxygen and ethylene, a chemical reaction of major economic importance [3,4]. The optical properties of silver nanoparticles or films, in or on Si, are attracting attention for possible applications in photovoltaics [5], fiber optics [6], and photonic band gap devices [7]. In addition to its optical properties, silver is attractive in such technologies because it is immiscible with silicon, a feature that is unusual among metals.

The goal of the present work is to determine the effect of oxygen on the stability of Ag islands supported on Si(111), and specifically whether these islands react differently to oxygen exposure, depending on their height. For Ag on Si(111)-7×7, it is believed that a quantum size effect (QSE) preferentially stabilizes Ag islands that are two layers high [8–10]. However, there have been no studies to determine how these Ag islands may respond to an oxygen-rich environment.

The Ag/Si(111)-7×7 system (without oxygen) has been studied extensively [8–18]. Up to a coverage of 0.5–0.6 monolayers (ML), Ag forms an irregular wetting layer (WL) in which the Ag is nonmetallic, and remnants of the original Si(111)-7×7 are exposed [9,12,17]. After the WL saturates at 0.5–0.6 ML, excess Ag aggregates as taller islands. Fig. 1 is a schematic that defines the various structures on this surface, and the nomenclature used in this paper.

The Ag island height distribution depends on deposition conditions [9,16]. Two-layer islands are favored most strongly when Ag is deposited below 300 K and annealed. A more heterogeneous distribution is obtained (presumably because of kinetic limitations) by deposition of Ag at 300 K, and this is desirable for the present purpose because it allows in situ comparison of islands with different heights.

There have been two previous studies of the interaction of oxygen with Ag/Si(111)-7×7 [17,19]. Unlike the present work, they did not focus on Ag coverages high enough to produce QSE-stabilized islands, but rather on low Ag coverages corresponding to a partially-filled WL. The most extensive report was from Zhang et al. [17] who used scanning tunneling microscopy (STM), photoelectron spectroscopy, and vibrational spectroscopy. They found that oxygen adsorbs selectively on Si. However, even a very low coverage of Ag (0.06 ML) alters the surface electronic states of Si, and suppresses oxygen adsorption beyond that expected from simple site-blocking. Furthermore, they reported that co-adsorbed Ag changes the binding mode of atomic oxygen pairs. On clean Si(111)-7×7, it had been established that oxygen adsorbs dissociatively, forming localized pairs of atoms that can bind to Si in two distinct configurations [17,20–22]. In one configuration, both oxygen atoms insert into Si–Si pi bonds, and in the other, less-stable configuration, only one oxygen atom inserts into a Si–Si pi bond, while the other adsorbs atop a single a Si atom. Zhang et al. [17] found that co-adsorbed Ag promotes the latter configuration, and suggested that the driving force is stronger Ag interaction with the adsorbed form of atomic oxygen.

2. Experimental and computational details

Experiments were performed in an Omicron variable-temperature STM system described elsewhere [23]. Chamber base pressure did not

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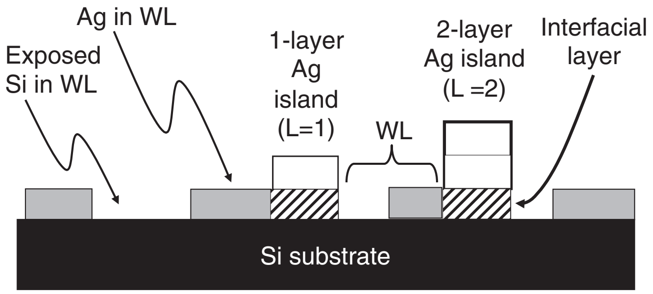

Fig. 1. Schematic showing the different types of surfaces and Ag layers in this system. WL stands for wetting layer, and the height of a Ag island above the WL is indexed by L.

exceed 1.5×10^{-8} Pa throughout the procedures, including Ag evaporation. The Si sample was p-type, boron-doped, with resistivity of 0.02 Ω cm. We prepared the Si(111)-7×7 surface according to standard procedures [24–26]. Ag was deposited at 300 K. The sample was exposed to oxygen, also at 300 K, by back-filling the chamber through a leak valve. Oxygen pressures were in the range 2×10^{-8} to 4×10^{-7} Pa. Exposures are given in Langmuirs (L), where $1\ \text{L}=1.3\times10^{-4}$ Pa s. During oxygen exposure the STM tip was usually withdrawn to avoid possible shadowing effects, and so the same region was not imaged before and after oxygen exposure. The total Ag coverage, θ_{Ag}, was calculated from STM images on the basis of the areas of different types of features. For this purpose, it was assumed that the Ag coverage in the WL was 0.5 ML, and in the interfacial layer and in each upper layer of a Ag island, local coverage was assumed to be 1.0 ML. Using this calibration, islands emerged (by definition) above 0.5 ML. Islands were identified and analyzed in the STM images, using WsXM software [27]. Typically, acquired image sizes were 250×250 nm^2, because this afforded a good compromise between statistics (capturing many islands in a single image) and accuracy (being able to identify all islands, even the smallest, and measure their dimensions). The z-piezoelectric calibration was checked by measuring the known step height of Si(111). Positive tip bias, V_b, corresponds to a filled-states image.

We found that Ag island density can be measurably different close to step edges than in the middle of terraces, so the present discussion and analysis is restricted to areas that were at least 250 nm away from a step edge.

Two main types of experiments were performed: a control experiment, and an oxygen exposure experiment. In both cases, Ag was first deposited on the surface. At a time 1.3 to 1.7 h after the start of Ag deposition, an initial set of STM images was captured. Next, the sample was either allowed to age in UHV (control experiment) or was exposed to oxygen during the equivalent period. A final set of images was then acquired, such that the total time elapsed between the start of deposition and the second set of images was 2.7 to 3.0 h. Every effort was made to ensure that the control and oxygen-exposure experiments were identical except for the way the sample was treated between the two imaging phases.

First-principles calculations were performed using the generalized gradient approximation (GGA) in the formulation by Perdew–Burke–Ernzerhof (PBE) [28] implemented in the Vienna ab initio simulation package (VASP) [29–31]. Valence electrons were treated explicitly and their interactions with ionic cores were described by Projector Augmented Wave (PAW) pseudopotentials [32,33]. Lattice constants obtained from these calculations were 0.547 nm for Si and 0.416 nm for Ag, using the PAW-PBE under density functional theory (DFT). Supercells of a 4×4 Ag(111) film on a 3×3 Si(111) substrate, consisting of two bilayers of Si passivated by hydrogen at the bottom (Fig. 2), were used in the calculations. The lateral dimension of the (3×3) Si(111) substrate (1.160 nm) was close to the lateral dimension (1.176 nm) of a (4×4) Ag cell. Therefore, the lattice mismatch effects due to the use of periodic boundary conditions in the calculations should be small. The dimension of the supercell in the z direction was 3.5 nm, which allowed a vacuum region of about 2 nm to separate the atoms in the supercell and their replicas. The wave functions were expanded in a plane wave basis set with an energy cut-off of 250 eV. A k-point grid of 3×3 Monkhorst–Pack type was used for the surface Brillouin zone. All atoms in the supercell were allowed to relax until the forces on each atom were smaller than 0.02 eV/nm.

3. Experimental results

First consider the effect of oxygen on the WL, which is shown in Fig. 3. In Fig. 3(A), the large bright feature is a 2-layer Ag island, surrounded by WL. Before oxygen exposure, the Si(111)-7×7 unit cell can be resolved in the WL, as shown in Fig. 3(B), where its unit cell (somewhat distorted) is outlined. The brighter, more amorphous regions are Ag in the WL. Fig. 3(C–D) shows similar images after oxygen exposure. The 7×7 is no longer visible, and the features in the WL are less defined.

Oxygen exposure affects not only the qualitative appearance of features in the WL, but also the quantitative vertical roughness. We measure WL roughness using images with areas of at least 25 nm^2 (without Ag islands), since below this size threshold, roughness depends on image size and hence is not a robust parameter. The root-mean-square (RMS) roughness of the WL consistently increases after oxygen exposure, by ~0.02 nm (by ~30 to 50%), whereas it does not change significantly when the clean surface is simply aged over the same time period. This is quantitatively true for both positive and negative values of V_b.

Consider next the Ag islands. Fig. 4 shows representative STM images from a pair of experiments consisting of a control, and 100 L oxygen exposure. In both experiments, θ_{Ag}~0.6 ML. Fig. 5 shows similar data but here θ_{Ag} is higher, ~ 1.4 ML. Because of the higher θ_{Ag}, islands in Fig. 5 have larger area than in Fig. 4, but their number density is about the same. Another consequence of the higher θ_{Ag} is that almost all the islands in Fig. 5 are initially 2-layer, whereas in Fig. 4, the majority are initially 1-layer. In both figures, the final images from the control experiment are visually similar to those from the oxygen exposure experiment. Clearly, many Ag islands survive oxygen exposure.

There is no evidence for oxygen adsorption on the tops of Ag islands. Fig. 6 compares high-resolution, Fourier-filtered [34] images of Ag islands before and after oxygen exposure. The roughness can be attributed to the underlying Si(111)-7×7 interface. On some island tops, the 7×7 can even be resolved [8]. There is essentially no difference between the two sets of images. The island tops are too small for quantitative roughness analysis, like that done for the WL. The conclusion that oxygen does not adsorb significantly on top of Ag islands is in complete agreement with the expectations from DFT presented in Section 4 below.

The Ag island height distribution is also of interest. Island heights are determined from individual island profiles. Several examples are shown in Fig. 7. We typically take the reference point to be the qualitative average of the wetting layer, as shown in the figure. On the clean surface, this yields the Ag island heights shown in Table 1 in the rows labeled with 0 L oxygen exposure. These values are physically-reasonable for 1-, 2-, and 3-layer islands [8]. After oxygen exposure, we choose again the average WL as baseline. This choice of baseline yields the island heights shown in Table 1 in the rows labeled with 100 L oxygen exposure. Islands can be classified as 1-, 2-, 3-, and 4-layers high, and their heights compare very well with clean surface values. The values in the Table were not dependent on whether the bias voltage was ±1 V, within the uncertainties given. This suggests that the heights primarily reflect topographic features.

Figs. 8 and 9 show N_L, the number density of Ag islands of various heights, corresponding to Figs. 4 and 5, respectively. In the control experiment of Fig. 8(A–B), all island densities decrease with time, but the relative population of 2-layer islands increases at the expense of 1-layer islands. These observations indicate that the Ag island ensemble coarsens significantly on a timescale of a few hours, at 300 K and