Novel Growth of Ag Islands on Si(111): Plateaus with a Singular Height

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Growth and transport properties of thin Ag films on Si(111) are investigated by scanning tunneling microscopy and *in situ* resistivity measurements. At low coverage, the Ag adatoms form isolated islands with a strongly preferred height and flat tops, rather than commonly observed pyramids. Such plateaus increase their lateral extent with coverage *without* changing height, forming a percolated network with sharply reduced resistivity above a critical coverage. This behavior suggests how the quantized electrons confined in the Ag islands could influence the growth, and may provide a unique pathway to prepare nanometer-scale structures with intriguing mesoscopic properties. [S0031-9007(98)08044-2]

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Growth of metal films on semiconductor substrates has been the subject of extensive experimental and theoretical studies over the decades [1]. Because the potential of well-ordered structures in electronic, magnetic, or optical device applications depends sensitively on their size and spatial distributions, it is highly desirable to achieve sharply defined length scales in such systems. Because of stress effects, the most commonly observed growth mode for nonreactive metals/semiconductor interfaces is the formation of three-dimensional (3D) islands with widely varying heights, either on the clean substrate (Volmer-Weber growth) or after the completion of a few wetting layers [Stranski-Krastanov (SK) growth] [2–8]. To obtain well-ordered structures, previous efforts have focused primarily on two opposite growth regimes. One effort is directed toward growth of two-dimensional (2D) or flat films with abrupt metal/semiconductor interfaces [3,9,10] as ideal testing grounds for theoretical concepts [11–13] and other electronic or transport properties [14–16]. The goal of the other effort is to grow ordered nanometer-scale 3D structures (quantum wires or dots) [17,18]. Very recently, a novel "electronic growth" mechanism has been developed theoretically for such systems, in which the energy contribution of the quantized electrons confined in the metal overlayer can actually determine the morphology of the growing film, prevailing over the strain energy [19,20].

In this Letter, we report the observation of an intriguing growth mode in a model system, Ag on Si(111), achieved through a two-step process devised to explore the possible quantum nature of the growth morphology and the corresponding transport properties. 3D plateaulike metal islands with a strongly preferred height are observed when Ag is deposited at 150 K and subsequently annealed to room temperature (RT). The islands increase their number density and lateral extension with coverage with no change in height, eventually forming a percolated network of the same preferred height. *In situ* conductivity measurements indicate a sharply reduced film resistivity above a critical coverage, much higher than what was previously observed at low temperature (LT) without annealing [16,21]. The present work makes a plausible case that, during the two-step growth process, the electronic driving force can play a dominant role in the evolution of the film growth, leading to the unique plateaulike morphology with intriguing transport properties.

Ag/Si(111)-(7×7) is a prototypical nonreactive metal/semiconductor interface, which follows the SK growth mode for RT Ag deposition [2,6–8,22]. For LT deposition, reflection high-energy electron diffraction oscillations were observed up to many monolayers [23,24], and scanning tunneling microscope (STM) images indicated quasi-layer-by-layer growth up to 3.6 ML, attributed to the lower average island size and higher island density compared to the RT case [21]. Transport measurements of LT-deposited Ag films ($T < 80$ K) revealed an increase in the conductivity at 0.85 ML [16], caused by the formation of a percolated structure at this coverage [16,21]. Although many studies have dealt with the effect of temperature and deposition rate on the growth mode, no systematic study has been carried out to document changes of the growth mode as a function of annealing temperature.

In this work, n-type doped (1–500 Ω cm) (111) silicon wafers were used for both STM and transport measurements. The samples were cleaned in ultrahigh vacuum (base pressure 1×10^{-10} torr) by several flashes to 1500 K, followed by slow cooling, to obtain a clean (7×7) surface with a low step density. Silver was evaporated from a molybdenum crucible with a flux rate varying from 0.3 to 3 ML/min [1 monolayer (ML) is equivalent to the nominal surface atomic density of Ag(111), 1.5×10^{15} atoms/cm^2, as in Ref. [21]]. The conductivity measurements were performed under similar sample conditions by monitoring the voltage drop across a pair of wires in elastic contact with the surface, while a constant current of less than 30 μA was supplied through the wafer, similar to prior studies [25].

Figure 1(a) is a typical STM topography image for a 1-ML Ag film, deposited at 150 K and annealed to 300 K.

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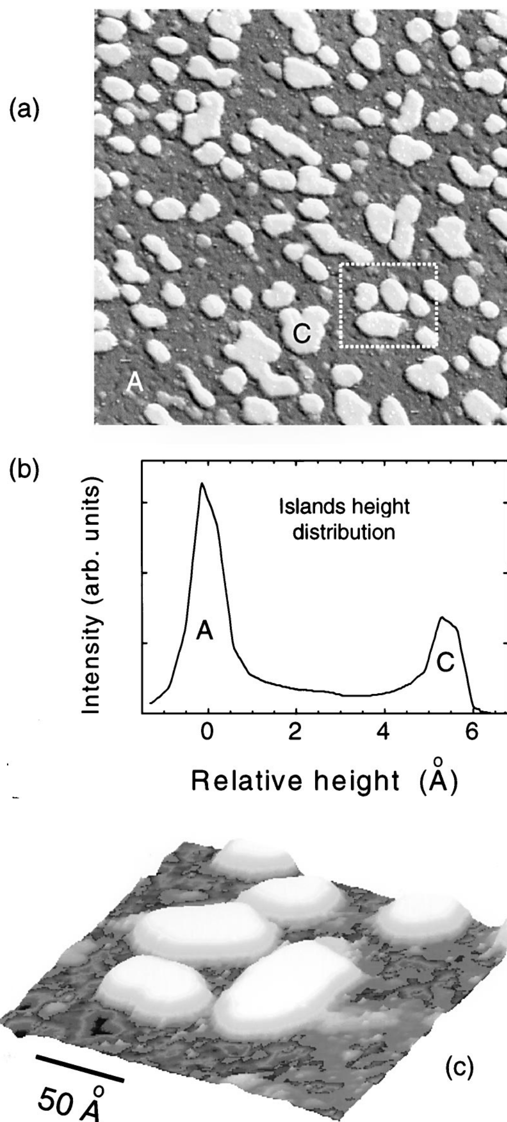

FIG. 1. (a) STM topography for a 1-ML Ag film deposited on Si(111) at 150 K and annealed to room temperature (image size: 1000×1000 Å^2). (b) Island height distribution obtained from (a), showing the strongly preferred height C of the islands. The intensity of peak A represents the Ag wetting layer. (c) Three-dimensional view of the area marked in (a), showing the flatness on top of the plateau islands.

The dark background area (A) is the first Ag layer, on top of the Si(111) surface. Since the clean Si surface density is half that of the Ag(111) surface density, the first layer corresponds to a Ag amount equal to 0.5 ML. The brightest features (C) are flat silver islands. The island height distribution obtained from the image is shown in Fig. 1(b), where the height is measured relative to the lower Ag layer. Besides the main peak associated with the wetting layer A, the curve clearly shows that all the 3D Ag islands have only a single preferred height of about 5.4 Å. Assuming that the interlayer spacing of the Ag islands is close to its bulk value along the (111) direction, each island contains two Ag layers. Remarkably, the root-mean-square roughness of the height distribution of any given island reveals that the top of the island is very flat: $w_{\mathrm{rms}} = 0.26$ Å, which is clearly illustrated in Fig. 1(c). Nevertheless, for the whole image one obtains $w_{\mathrm{rms}} = 2.6$ Å, indicating that the surface morphology on a larger scale is still quite rough.

The formation of such plateaulike islands with one single preferred height shows the novelty of this growth mode when compared to the formation of islands of multiple heights and pyramids typical of many metal/semiconductor interfaces [3–5,8,17]. An obvious question follows: Will the double-layer islands persist as the film grows, eventually coalescing while keeping the same preferred height?

The typical morphology of a 2.2-ML Ag film deposited at 150 K and annealed to RT is shown in Fig. 2(a). One striking feature is the presence of a connected network of the islands, resembling a percolated structure. In fact, starting from any two points located on two opposite edges of the image, it is possible to find a connecting path through the layer, as represented by the dotted line in the figure. The corresponding island height distribution profile, shown

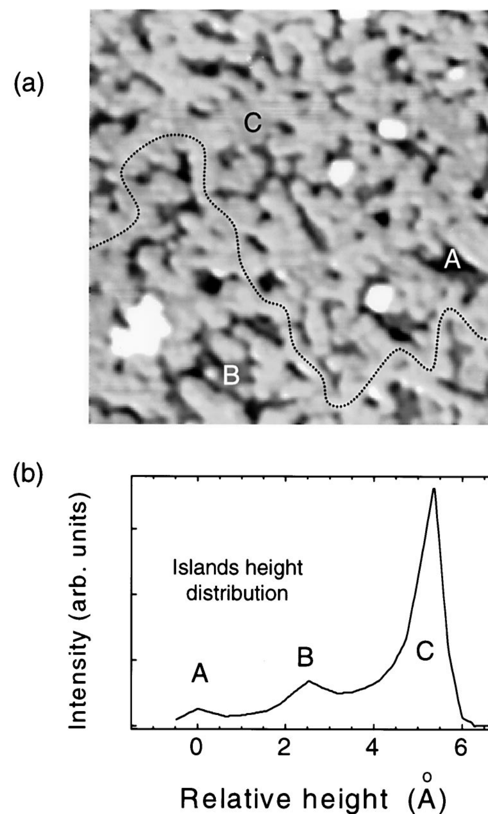

FIG. 2. (a) STM topography for a 2.2-ML Ag film deposited on Si(111) at 150 K and annealed to room temperature (image size: 1000×1000 Å^2), showing the presence of a percolated network, as indicated by the dotted line. (b) Island height distribution obtained from (a), indicating that the percolated network has the same height C as that of the plateaus shown in Fig. 1(a).

in Fig. 2(b), indicates clearly that the percolated layer also has the same preferred height as the plateaus labeled *C* in Fig. 1(a). This suggests that the formation of the percolated structure is achieved by an increase in density of such single-height islands, due to the same growth mode observed for lower coverages. The rms roughness on top of the percolated layer is again very low (0.28 Å).

The image shown in Fig. 2(a) also reveals the presence of a lower layer, whose intensity is indicated by the small peak *B* in Fig. 2(b). By either using a lower deposition rate at LT or annealing for longer periods at RT, we find that the weight of peak *B* will decrease, leaving the double-layer peak *C* only. Therefore, we conclude that the stable structure of the film at RT corresponds to the double-layer height, for the percolated structure as well as for the plateaulike islands. Notice that the plateau islands and the percolated network are only metastable: Upon annealing above 450 K, they both evolve into huge mounds and pyramids, similar to the structures of the SK growth mode.

A comparison of the film morphologies shown in Figs. 1(a) and 2(a) plus those obtained at intermediate coverages (not shown) leads to the following picture: Up to 0.5 ML, Ag strongly prefers to form a wetting layer on Si(111), but going beyond 0.5 ML, formation of 3D plateaulike islands with an unusually uniform height is strongly favored on top of the wetting layer. The islands increase their density and size as the coverage is further increased, but without changing the height, eventually forming the percolated network of the same preferred height.

The novel growth behavior reported here cannot be accounted for within the conventional SK growth model, in which the dominance of stress would lead to large islands with widely varying heights and a single-atomic-layer height increment [22]. In contrast, the two-step approach, namely, LT deposition followed by annealing to RT, leads to the double-atomic-layer-high islands observed here, effectively avoiding the thermodynamically favored SK growth mode. Within this mode, Tersoff and Tromp [17] developed a model predicting the formation of islands with a critical width and a trapezoidal or triangular cross section. Apparently, their model cannot be applied to the present case, because here the islands clearly have a strongly preferred height, but with random widths and irregular shapes in the lateral direction up to the percolation limit.

The novel growth mode shown here can be explained qualitatively using the simple growth model recently developed [19], stressing the possibility of preferred height selection in the film thickness. This model considers two main competing effects contributing to the total energy of the film. Quantum confinement of the electrons in the metal overlayer leads to an energy increase of the film; charge transfer from the metal to the substrate leads to an energy decrease. The competition between the two determines the behavior of the total energy curve as a function of film thickness and defines a critical thickness below which the film is unstable [19]. In order to circumvent the dominance of stress effect at RT and therewith the SK growth mode, the film has to be deposited under low adatom mobility conditions [19]. Upon annealing (and as a result of the increased atomic mobility), the film evolves away from its kinetically limited configuration by eliminating islands that are unstable, leading to the formation of the morphology observed here, i.e., the plateaulike islands and eventually the percolated network, both with the same preferred thickness. Further deposition of Ag will lead to the formation of an atomically flat film at the critical thickness, as experimentally observe recently [26]. We should emphasize that the application of the growth model of Ref. [19] is at this stage a rather qualitative explanation. First-principles-based calculations such as those in Ref. [27] but for the specific system of Ag growth on Si(111) are needed, in order to reach quantitative agreement with the experiment.

The morphological evolution of the Ag films influences dramatically the transport properties of the film, as shown in Fig. 3. Here the resistivity for films with Ag coverages up to 1 and 2.2 ML is plotted in Figs. 3(a) and 3(b), respectively. The voltage drop is normalized to the voltage V_0 measured on the clean Si(111)-(7 × 7) surface. Typical values of V_0 are ~10 mV, corresponding to the substrate resistivity in the 1–500 Ω cm range. Film depositions were carried out at $T = 150$ K, and the voltage drops were

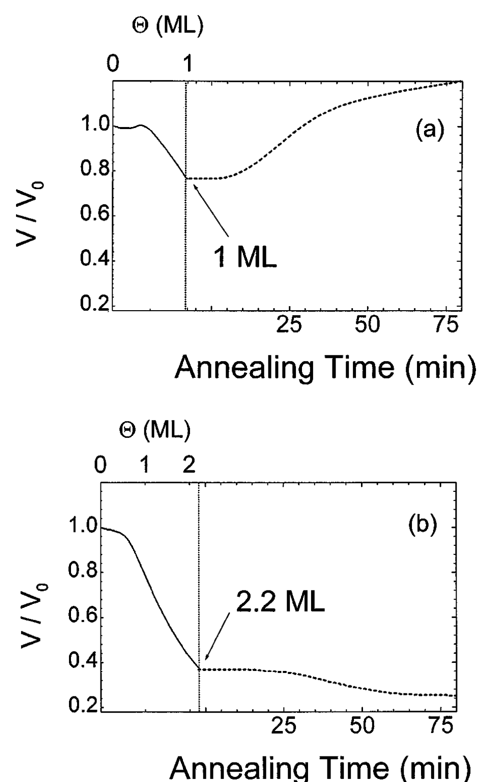

FIG. 3. Resistivity data as a function of deposition time (solid line) and of annealing time (dotted line) for a Ag film with total thickness of (a) 1 ML and (b) 2.2 ML.

monitored *in situ*. After an initial plateau, the voltage decreases to 75% of the initial value when the amount deposited is 1 ML [Fig. 3(a)]. The voltage drops to 35% of the initial value when the coverage reaches 2.2 ML [Fig. 3(b)], indicating higher film conductivity.

After depositions of the Ag films, the voltage changes were monitored while the systems were annealed to RT. Dramatically different behaviors were observed in the two cases. The resistivity of the 2.2-ML film further improves during annealing [Fig. 3(b)], dropping finally to 28% of the initial value. From a simple circuit analysis for the combined substrate-film system, we conclude that the film resistivity is 5×10^{-5} Ω cm, consistent with similar analyses [14,16,25]. However, the 1-ML film showed the opposite trend: The voltage increased with increasing temperature, saturating to a value even higher than the initial value of the clean substrate.

The opposite behavior of the film resistivity during the annealing at the two Ag coverages is consistent with their morphological differences observed by the STM. Apparently, the percolated network of the 2.2-ML film contributes significantly to the conductivity, while the nonconnected plateau islands in the 1-ML film do not; to the contrary, the accumulation of Ag atoms in forming these plateaus even leads to a reduced conductivity. Notice that the percolation coverage observed here is significantly higher than what was observed previously for the case of LT deposition without RT annealing [16,21].

In summary, the present work provides plausible evidence that during the two-step growth process the electronic driving force can play a dominant role in the evolution of the growth system, leading to the unique plateaulike islands with a strongly preferred height of about 5.4 Å and intriguing transport properties. In particular, the percolation transition in the metal network is established at 2.2 ML, as confirmed by its sharply reduced resistivity. The growth mode demonstrated here explores the interplay between growth kinetics and a novel thermodynamic driving force, and cannot by simply classified into any of the three commonly known growth modes. Furthermore, the present work demonstrates the potential of first designing nanometer-scale structures in the regime governed by the quantum laws, then using those structures as ideal testing grounds to explore other quantum phenomena such as phase coherence in transport.

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