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Epitaxial growth of gold on Si(001)

Martin Wölz [a], Yue-Lin Huang [b,*], Michael Seibt [c], Steven C. Erwin [d]

[a] Paul-Drude-Institut für Festkörperelektronik, 10117 Berlin, Germany
[b] Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan
[c] IV. Physikalisches Institut, Georg-August-Universität Göttingen, 37077 Göttingen, Germany
[d] Center for Computational Materials Science, Naval Research Laboratory, Washington, D.C. 20375, USA

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ABSTRACT

We study the formation of nanoscale epitaxial Au islands on Si(001) below the eutectic point. Growth experiments were performed in molecular beam epitaxy, and plausible interface models were derived from electron diffraction and transmission electron microscopy. For these models, formation energies were obtained in density functional theory (DFT). In-situ electron diffraction indicates that during the deposition of the first two monolayers, the Si(001) surface mesh is preserved. Au(110) islands form at a coverage above three monolayers. DFT shows that the formation energy for an atomically flat interface is higher for this (110) orientation than for (001) growth. We propose an interface configuration that promotes Au(110) growth and is kinetically stabilized even though this is not the epitaxial orientation with the lowest mismatch strain. The proposed configuration implies a mixed interface layer containing both Au and Si atoms.

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1. Introduction

The creation of metal nanostructures by self-assembly has become an important activity in many research and application fields. Metal nanostructures offer tunable optical, electronic, and catalytic properties [1–4], as well as compatibility with bio-sensing and functionalization [5–7]. Their integration with semiconductor surfaces is not only interesting from a fundamental physics perspective [8,9] but also important for the success of future nanoelectronics. In particular, a detailed understanding—at the atomic level—of the structure of metal/semiconductor interfaces may be important for optimizing and controlling nanoscale devices. Despite many studies of metallic thin films [10–13] and nanostructures [14] grown on semiconductor substrates, little is understood in detail regarding the formation of their epitaxial interfaces. One complication is the tendency toward intermixing at metal/silicon interfaces [10]. This intermixing includes interdiffusion as well as the formation of intermetallic compounds [15] in the form of equilibrium or metastable silicides [16,17]. Intermixing presents a difficult challenge for the preparation of a well-defined, atomically sharp metal/semiconductor interface. Indeed, such complications may have played an important detrimental role in early attempts to understand the relationship of Schottky barrier heights and Fermi-level pinning [18].

Au, Al, and Ag constitute a group of face-centered cubic metals that form a binary eutectic with Si. Epitaxial growth of these metals on Si has been reported in several papers [19]. Epitaxy is somewhat surprising for these systems because the bulk lattice mismatch would place the metal film under 33% tensile strain in cube-on-cube growth. For example, Al(111) films grow epitaxially on Si(111) substrates, and the lattice mismatch is then accommodated by a regular network of edge dislocations that provide an interface registry of 3 Si atoms to 4 metal atoms [20], resulting in a coincidence site lattice (CSL) with a very low mismatch strain. Such a CSL is not observed in the (001) plane [19], however, proving that purely geometric considerations do not explain the resulting epitaxy. The growth mode is dependent on both temperature and deposition rate [21], and hence kinetics, as well as thermodynamics, must be included in a complete description of the formation of Au/Si epitaxial interfaces.

Recent studies of epitaxial gold nanostructures on silicon have investigated the structure of the Au/Si interface formed upon cooling the Au–Si melt from high temperature [14,22]. Few studies have focused on the growth of Au on Si at temperatures below the eutectic point ($T_e = 636$ K, $x_{Si} = 18.6$ at.%), where Au does not react with Si, and the formation of a metal film on a Si substrate is thermodynamically possible. Au films grown on Si(111) at room temperature have been reported to change their orientational relationship upon thermal annealing [23]. When much higher deposition rates were used, epitaxial growth of Au/Si(111) did not occur at all (at most deposition temperatures) [19].

The available reports on the crystal growth of Au on Si(001) do not give a conclusive picture of the atomic interface structure. At 12 K, single

* Corresponding author. Tel.: +886 3 863 3728.
E-mail addresses: huang_yuelin@mail.ndhu.edu.tw (Y.-L. Huang), steve.erwin@nrl.navy.mil (S.C. Erwin).

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Au atoms adsorb along the dimer rows of the reconstructed Si(001)2 × 1 surface [24,25]. This may also be the case at 5 °C, where the reconstruction is known to disappear only at a Au coverage of half a monolayer (ML) [26–28]. Several studies found the Si surface mesh to remain unperturbed up to a Au coverage of 2 ML [26,27]. Then an interface reaction sets in that intermixes Au and Si [27,29], a process also known as 'Si outdiffusion' [30]. At higher coverages, a Au(111) texture with random in-plane orientation is obtained at room temperature [31,28]. At elevated temperatures as high as 200 °C, epitaxial Au(110) films have been observed to form on Si(100) under flash deposition in high-vacuum conditions [19]. In these epitaxial films there are two equivalent in-plane orientations Au(110)[001] ∥ Si(001)⟨110⟩, and the resulting structure is sometimes called a 'mazed bicrystal'.

Our previous studies of Au/Si(001) interfaces showed that two different epitaxial relationships can occur, depending on whether the disordered Au–Si precursor phase is created by cooling a high-temperature melt or by allowing reactions between the film and substrate at temperatures below the eutectic point [32]. Using molecular-beam epitaxy (MBE) with Au and Si co-deposition, we showed that Au(110) epitaxy can be achieved on well-defined Si(001) surfaces at temperatures between 65 °C and 260 °C [28]. Temperature changes within this range did not lead to changes of the preferred epitaxial orientation. The epitaxial Au(110) growth is kinetically stabilized: on the one hand, the epitaxial interface formation is enhanced by the simultaneous supply of Si adatoms during Au deposition ('deposition-induced epitaxy'). On the other hand, this orientation relationship is not obtained when an Au film forms on Si(001) by precipitating from an alloy melt ('solidification-induced epitaxy') [32,14].

In the present study, we analyze the role played by kinetics during the formation of epitaxial Au/Si(001) interfaces formed by deposition at low temperature. Our results show that the preferred crystallographic orientation of Au on Si(001) depends on the Au coverage: for very low coverage Au(001) is preferred, while at higher coverage Au(110) is preferred. We combine in-situ studies of the evolution of the crystal surface structure, ex-situ microscopy results, and kinetic considerations to obtain Au/Si interface models. Density-functional theory (DFT) calculations comparing the formation energies of the proposed epitaxial interfaces support the observations and shed light on their underlying cause.

2. In-situ study of Au island formation on Si(001)

Substrates were prepared from *p*-Si(001) with a resistivity of 10 Ωcm by removing organic contaminants in a piranha etch and a subsequent HF dip. A controlled oxide layer was then applied by boiling the samples in methanol. After loading a sample to the MBE chamber and outgassing the holder, the oxide was evaporated at 900 °C. Any possible remaining foreign atoms at the surface were covered by growing a 200 Å Si buffer layer and annealing at 1050 °C. The growth chamber pressure during the deposition was between 10^{-9} mbar and 10^{-7} mbar. The evolution of the surface structure was studied in situ by reflection high-energy electron diffraction (RHEED). The substrate temperature was controlled by a thermocouple, which was calibrated by repeated observations of the RHEED contrast disappearing upon heating a Au/Si film to the eutectic temperature. During the MBE growth experiments, atomic fluxes of Au and Si were supplied by electron beam evaporators and controlled with quartz crystal microbalances, calibrated to the growth rate of pure Au and Si films (in Å/s). Since we are interested in the epitaxial growth of Au with respect to the Si lattice, we report the total amount of deposited Au (Θ_{Au}) in monolayers (ML) with respect to the areal density of Si atoms in the unreconstructed Si(001) surface: 1 Å of equivalent Au film thickness corresponds to 0.869 ML. The frequency of RHEED oscillations observed during layer-by-layer growth of Si(001) and Au on Si(001) were in quantitative agreement with the calibrated deposition rates [28]. Next we turn to the information about the sample surface that can be obtained from the evolution of the RHEED pattern.

2.1. Initial phase of pure Au deposition

We investigated the first stage of growth of Au on Si(001) at 5 °C in an experiment with deposition of pure Au at 0.16 ML/s [28]. Fig. 1 (a) and (b) show the evolution of the RHEED contrast and intensity in the areas of the diffraction pattern indicated in Fig. 1(c). The contrast is defined as the variance of the brightness in these areas around diffraction spots. The clean Si(001) surface is characterized by the 2 × 1 reconstruction which gives rise to the half-order reflection $\frac{1}{2}0$. The reconstruction disappears under Au irradiation, indicated by the disappearance of the one-half ML [26]. An important observation is that the RHEED intensity of the 00 and 10 reflections oscillates twice under Au irradiation before the RHEED pattern completely vanishes. This means that the Si(001)1 × 1 surface structure is restored when the complete coverage of 1 ML and 2 ML of Au is achieved. Further pseudomorphic growth does not occur: starting at a coverage of about 3 ML, no diffraction contrast is observed. In agreement with previous reports on outdiffusion of Si and surface silicide formation [30], we consider the surface to be amorphous at this stage.

2.2. In-situ study of Au:Si co-deposition on Si(001)

Au(110) epitaxy can result from the deposition of Au onto Si(001) [33,19,28]. The temperature range in which this epitaxial orientation occurs in MBE is between 65 and 260 °C when Au:Si co-deposition is employed [28]. We describe here an experiment with Au and Si co-

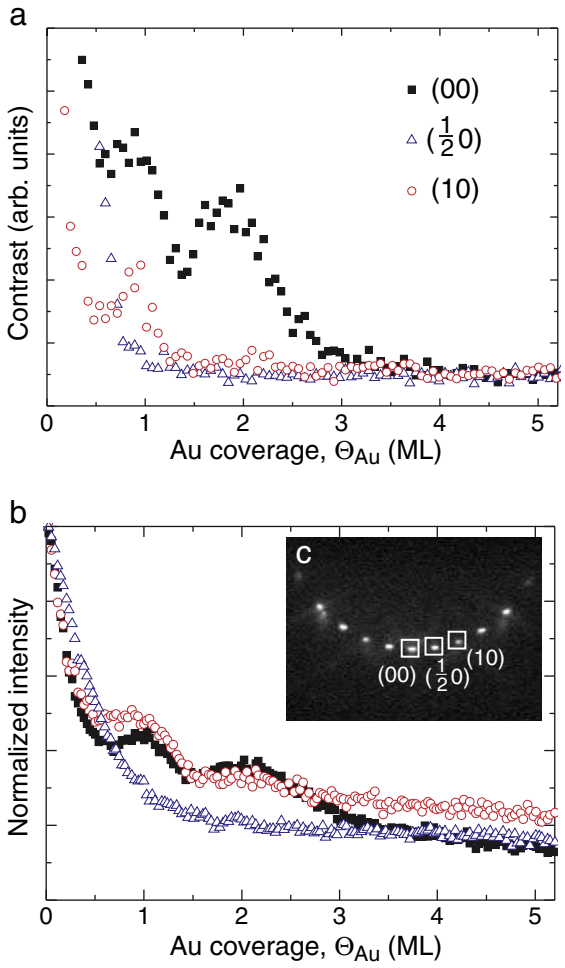

Fig. 1. RHEED intensity in the Si[110] azimuth during the initial phase of Au deposition on Si(001). (a) Contrast. (b) Normalized intensity. The integration areas around the reflections on the RHEED screen are marked in the image (c), acquired prior to deposition.