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ScienceDirect
Surface Science 602 (2008) 391–398
SURFACE SCIENCE
www.elsevier.com/locate/susc

Multi-mode growth in Cu/Si(1 1 1) system: Magic nanoclustering, layer-by-layer epitaxy and nanowire formation

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Received 17 August 2007; accepted for publication 22 October 2007
Available online 26 October 2007

Abstract

Using scanning tunneling microscopy and low energy electron diffraction, we have studied formation of the Cu/Si(1 1 1) interface. It has been found that depending on the growth conditions the various types of nanostructures can be formed. Room-temperature deposition of the Cu submonolayers onto the Si(1 1 1)7×7 surface results in formation of the ordered arrays of identical-size magic clusters. Room-temperature deposition of Cu onto the Si(1 1 1)5.55×5.55-Cu surface phase leads to developing arrays of Cu nanowires due to Cu accumulation at the atomic step edges. When Cu is deposited onto the Si(1 1 1)5.55×5.55-Cu surface held at 100 K, layer-by-layer growth of the epitaxial Cu(1 1 1) film takes place, after which it changes to the growth of 3D Cu islands having a shape of truncated pyramides.

Keywords: Atom–solid interactions; Silicon; Copper; Surface structure, morphology, roughness, and topography; Scanning tunneling microscopy (STM), Low energy electron diffraction (LEED)

1. Introduction

Growth of Cu on Si(1 1 1) has been a subject of extensive research not only due to the basic scientific interest but also due to its technological significance as one of the most relevant metal-semiconductor interfaces for modern device technology. Peculiar feature of the Cu/Si(1 1 1) interface is the large lattice misfit of about 15%. At the interface, silicide layer is known to be formed which plays a key role in overcoming the large lattice mismatch [1–4]. The interlayer thickness varies from a few to a dozen monolayers depending on the growth temperature [2–4]. On top of the silicide interlayer, an epitaxial Cu(1 1 1) film grows in the layer-by-layer-like fashion, albeit not ideal. Thus, quality of the extra-thin epitaxial Cu(1 1 1) films grown on the Si(1 1 1)7×7 surface suffer from both the presence of the silicide layer at the interface and the roughness of the outer surface [5]. In the present study, we have found that perfection of the Cu(1 1 1) films is considerably improved if they are grown on the Si(1 1 1)5.55×5.55-Cu surface phase at low-temperatures. In this case, from two to five epitaxial Cu(1 1 1) monolayers can be grown in an ideal layer-by-layer fashion. Moreover, using the Si(1 1 1)5.55×5.55-Cu surface phase as a template one can form the Cu nanowire arrays, since at room temperature the deposited Cu adatoms are free to migrate over terraces but become trapped at step edges. Thus, the results of the present study show how to use various growth conditions to form various types of Cu nanostructures on Si(1 1 1).

2. Experimental

Our experiments were performed with Omicron scanning tunneling microscope (STM) operating in an ultrahigh

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doi:10.1016/j.susc.2007.10.032

vacuum ($\sim 1 \times 10^{-10}$ Torr). Atomically-clean Si(1 1 1)7×7 surfaces were prepared *in situ* by flashing to 1280 °C after the samples were first degassed at 600 °C for several hours. Copper was deposited by resistive heating a tungsten filament wrapped with a Cu wire. A typical deposition rate was of about 0.5 monolayer/min. Cu deposition rate was evaluated in the experiments on the layer-by-layer Cu(1 1 1) growth, taking place upon Cu deposition onto Si(1 1 1)5.55×5.55-Cu surface phase held at low temperatures (to be discussed elsewhere in a detail). A monolayer (ML) in this paper corresponds to 7.8×10^{14} cm^{-2}, the density of the topmost Si atoms on the unreconstructed Si(1 1 1)1×1 surface. Note that one atomic layer of the Cu(1 1 1) contains 1.8×10^{15} cm^{-2} (i.e., 2.3 ML) of Cu atoms. During the Cu deposition, the samples were held at a fixed temperature ranging from a room temperature (RT) down to about 100 K. For low-temperature depositions, the samples were placed into a specially designed homemade stage, cooled by liquid nitrogen [6]. Temperature of the stage was measured by a thermocouple attached to it, which means that actual sample temperatures might be somewhat higher than the temperatures indicated in the paper. The stage design allows low-temperature low energy electron diffraction (LEED) observations of the sample surface, but for acquisition of STM images the samples were moved to a standard STM stage held at RT. Thus, one should bear in mind that such STM images display the surfaces which were prepared at low temperatures but then "annealed" at RT. For STM observations, electro-chemically etched tungsten tips cleaned by *in situ* heating were employed. The STM images were acquired in a constant-current mode.

3. Results and discussion

In presenting our results we will use the following scheme. As a starting point, we will consider a growth of the Cu films on Si(1 1 1)7×7 surface making references to the known literature data. In the next session we will discuss the structure and composition of the Si(1 1 1)5.55×5.55-Cu surface phase. Then we will present our data on the Cu growth on the Si(1 1 1)5.55×5.55-Cu surface. First, we will give a general overview of the growth phenomena, proceeding then to a more detailed description of the growth at low temperatures of ~100 K and at a room temperature.

3.1. Cu growth on Si(1 1 1)7×7

Results of our STM and LEED observations on Cu growth on Si(1 1 1)7×7 reflect all general trends reported for this system in literature. In particular, when Cu submonolayers (e.g., ~0.4 ML of Cu) are deposited onto Si(1 1 1)7×7 substrate held at RT, ordered arrays of magic clusters are formed at the surface (Fig. 1). Cluster formation was first detected in STM studies of 1990s [7,8], but only recently these clusters have been designated as magic

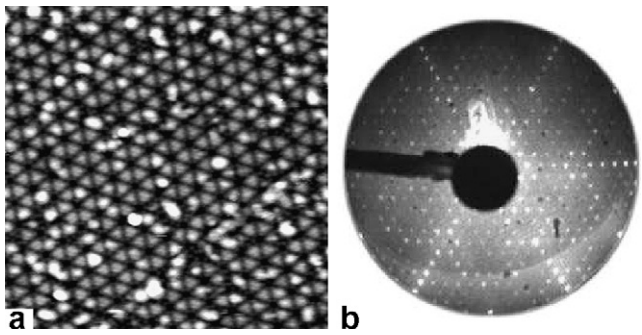

Fig. 1. (a) 420×420 Å^2 empty state (+2.0 V) STM image and (b) LEED pattern (E = 65 eV) from the magic cluster array prepared by deposition of 0.4 ML Cu onto the Si(1 1 1)7×7 surface held at RT.

clusters, i.e. the clusters having identical size and structure [9]. It should be noted that Cu cluster arrays are less perfect compared to those formed on Si(1 1 1)7×7 by Group III metals, Al [10,11], In [12] and Ga [13], which demonstrate an almost ideal ordering. In the case of Cu/Si(1 1 1)7×7 system ordered magic cluster arrays are depraved by a presence of the random clusters having irregular shape (Fig. 1a). In the present study, we have undergone several attempts to improve Cu/Si(1 1 1)7×7 magic cluster arrays by varying growth conditions, but unfortunately without a considerable success. In particular, the resultant surface structure does not depend greatly on the temperature of Cu adsorption (for example, magic cluster array can be formed even upon Cu deposition at 100 K followed by "annealing" at RT).

Fig. 2 presents a set of STM images acquired at various bias voltages from the same region of the Cu/Si(1 1 1)7×7 magic cluster array. One can see that STM appearance of the clusters varies greatly with varying bias voltage, indicating that the clusters are not built of Cu atoms only, but they comprise aggregations consisting of Cu and Si atoms. Remarkably, the bias dependence is different for clusters situated in the faulted and unfaulted halves of the 7×7 unit cell: at some sample voltages (−1.0 V, −0.5 V, +0.5 V, +2.0 V) they look identical, but at the other (+1.0 V, +1.5 V) drastically different. Atomic structure of the magic clusters has attracted a considerable interest of the researchers and for selected clusters (e.g., for those formed by Group III metals [12–18] or by sodium [19,20]) it has been successfully determined. For Cu magic cluster, Zhang et al. [9] suggested a model, in which six Cu adatoms form a ring-like aggregation with three sitting on the top of the Si center adatoms and three binding to the Si rest atoms. However, this model is tentative and not reliably justified. So, conclusive determination of the Cu magic cluster structure remains a challenging task for the researchers. We believe that a very peculiar bias-dependent STM appearance of the Cu clusters provides a hint for constructing structural models and could serve as a test for their validity upon comparing experimental and simulated STM images.

In agreement with the previously reported data [1–4], our STM and LEED observations reveal the following