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Formation and coalescence of surface domains introduced by metal deposition on a Si(111) surface

A.L. Chin, C.P. Chang, S.Y. Pai, I.M. Liu, G. Chern, F.K. Men *

Department of Physics, National Chung Cheng University, Chia-Yi 621, Taiwan, ROC

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ABSTRACT

By depositing sub-monolayer Au atoms onto a heated and slightly misaligned Si(111)-(7 × 7) surface, (5 × 2) stripes form on the upper step edges of terraces. Upon further heating, most of the terraces transform into either Au-free (7 × 7) terraces or fully reconstructed (5 × 2) terraces. By analyzing the distance distribution between neighboring (5 × 2) terraces, we have found the existence of an optimal distance between (5 × 2) terraces. This optimal distance, controllable via the Au coverage, can be explained by the minimization of long-range strain relaxation energy for a system consisted of alternating domains. The ability of tuning surface domain structure through metal deposition provides a new way of manipulating surface morphology in the nanometer-scale range.

1. Introduction

Driven by the desire to understand overlayer/interface properties as well as by the immense technological implications opened up through the ability of manipulating surface properties, surface scientists have studied the surface reconstructions introduced by metal deposition for many decades. [1] Not surprisingly, semiconductor surfaces as substrates for metal deposition attract special attention for their applications in modern electronic devices. [2] One example is the adsorption of Au on Si(111) where a series of structural transitions as a function of Au coverage has been discovered. The Au-induced reconstructions include, in the order of increasing Au coverage, the (5 × 2), [3,4] $\left(\sqrt{3}\times\sqrt{3}\right)$, [5–8] and (6 × 6) [5,8,9] reconstructions. In addition, one-dimensional (1D) Au atom chains have been observed on vicinal Si(111) surfaces, providing a rare opportunity to investigate the electronic properties of 1D system [10,11].

Surface stress has long been recognized as an important ingredient in determining the steady-state structure of a surface/interface. Some well-known examples include the growth of strained pseudomorphic layers in heteroepitaxy. [12,13] More recently, reports have demonstrated the effect of surface stress on the spontaneous formation of ordered elastic-stress domains. [14,15] Specifically, on a surface with orientationally inequivalent domains with anisotropic intrinsic surface stress tensors, such as the Si(001) surface, [16] a flat surface is unstable to the formation of a striped phase where a structure of alternating domains separated by domain boundaries prevails.

Many surfaces, unlike the Si(100) surface, do not possess orientationally inequivalent domains. As a result, using surface stress as a tool to manipulate the domain structure of a surface would be futile for a wide range of surfaces. It therefore would be desirable to investigate if, by varying the density of deposited metal atoms, controlled changes in the surface stress anisotropy can be achieved. This surface stress anisotropy would then lead to a periodic domain structure in a self-organized manner through the relaxation of long-range elastic energy, similar to what has been observed on the clean Si(100) surface.

Here in this paper we will show that, by depositing Au atoms onto a stepped Si(111)-(7 × 7) surface, a (5 × 2) reconstruction is formed as a narrow stripe by the surface step on most terraces. Upon heating, this intermediate stripe structure transforms into fully-reconstructed (5 × 2) terraces separated by (7 × 7) terraces. An optimal distance, controlled by Au coverage, between neighboring (5 × 2) terraces exists. The physics governing this optimal distance can be explained by the creation of a second type of elastic domain, the (5 × 2) terrace, on the surface which introduces an anisotropic surface stress tensor at the step, similar to the effect of two orientationally inequivalent domains on the Si(100) surface. [15] We will also demonstrate a scheme, by growing islands solely on the (5 × 2) terraces, that a patterned structure can be created in a self-assembled way.

2. Experimental details

Our experiment was carried out in an ultrahigh vacuum system with a base pressure of 1×10^{-10} mbar. Clean Si(111) surfaces with a miscut angle of 0.3° toward the [-211] direction were used as substrates. A fresh surface was cleaned by degassing at 700 °C via a DC current for several hours followed by heating to 1250 °C a few times for ~10 s each. No

* Corresponding author.
E-mail addresses: gchern@ccu.edu.tw (G. Chern), phymen@ccu.edu.tw (F.K. Men).

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effect due to the direction of the DC current relative to the sample surface was ever observed. The cleaned surface was then annealed at 900 °C for a few minutes followed by slow cooling to room temperature. The cooling rate was critical for obtaining a well-ordered (7 × 7) structure with low defect density, as examined by scanning tunnel microscopy(STM). A typical surface was consisted of (7 × 7) terraces averaging ~60 nm in width and separated by bi-layer height steps (0.31 nm in height) [17,18].

Au atoms were produced by heating a Mo crucible containing Au wire (99.99% pure) to ~1000 °C via electron bombardment. Co atoms, produced by heating a 2-mm-diameter Co rod (99.9% pure), were evaporated onto the Au-deposited surface at room temperature with a follow-up annealing. The deposition rates for both Au and Co were kept below 0.01 monolayer (ML, 1ML = 7.83×10^{14}atoms/cm^2, the unreconstructed Si(111) surface atom density) per second.

3. Results and discussion

After depositing ~0.07ML of Au at a rate of 0.03ML/min onto a stepped Si(111)-(7 × 7) surface at 600 °C, [19] the surface transformed into a structure where the upper edge of the step in most terraces reconstructed into a (5 × 2) structure, a structure typical for a Au-deposited Si(111) surface, as shown in the STM image on the left panel of Fig. 1(a). A side-view drawing was added to illustrate the relative positions between the (5 × 2) stripe, colored yellow, and the (7 × 7) domain within a terrace. In the STM images, the (5 × 2) reconstruction has a lower apparent height than that of the (7 × 7) structure despite both are on the same terrace.

To quantify the structural change in a terrace, we have plotted a histogram for 61 terraces where the number of terraces with their areal ratios of the (5 × 2) stripe to the (7 × 7) domain falling into a particular range is plotted against the areal ratio, as shown on the right panel of Fig. 1(a). 0 and 1 on the *x*-axis are for a terrace fully covered by (7 × 7) and (5 × 2), respectively. Note that, after Au deposition, only 4 out of 61 terraces were free of (5 × 2) stripes [20].

In order to examine the kinetics of the structural transformation, we continued heating the surface at 600 °C after the completion of Au deposition. Fig. 1(b) and (c) shows the STM images and the histograms of the areal ratio distribution after 30 and 270 s of heating, respectively. Since the number of terraces with areal ratios between 0 and 1 decreases rapidly, a trend of coalescing (5 × 2) stripes into complete (5 × 2) terraces was clearly at work. In order to form complete (5 × 2) terraces, Au atoms would have to travel across a number of (7 × 7) terraces.

By acquiring many STM images similar to that shown in Fig. 1(c) we are able to estimate the amount of deposited Au by taking the ratio of the total widths of all (5 × 2) stripes to the total widths of all terraces. We have obtained an Au coverage of ~0.09ML, in line with the value of ~0.07ML estimated from the assumption of 0.5ML saturation coverage for the (5 × 2) reconstruction. [21] This agreement implies that the total number of deposited Au atoms is conserved in the heating process. Please note that the width discrepancy in the (5 × 2) stripes between Fig. 1(a) and (c) is due to the limited size of STM images. As shown in the right panel of Fig. 1(c), there are many more terraces which are fully (7 × 7)-covered than those covered by (5 × 2).

In Fig. 1(d) we summarize the results of the kinetics experiments by plotting the fraction of the terraces having a mixture of (5 × 2) stripe and (7 × 7) domain as a function of heating time. A linear fit of the data points to the relation $\ln[\text{Fraction}(t)] \propto -t/\tau$, where τ is a time constant, is shown as the blue line. The inverse of the slope of the straight line gives $\tau = 135 \pm 10$s. The agreement between the data and the fit shows that the kinetics of approaching the steady state follows a simple exponential relaxation with a thermally activated time constant [22].

We have also worked on different Au coverages up to 0.2ML. Identical behaviors on the formation and the coalescence of (5 × 2) stripes were observed in those experiments. One set of experiment is shown in Fig. 2 where a surface with an Au coverage of ~0.2ML was prepared at 600 °C, as shown in Fig. 2(a). After 60 s heating at 600 °C, the (5 × 2) stripes in individual terraces coalesce as indicated in Fig. 2(b). We have found that the suitable temperature range for doing this experiment is roughly between 600 and 700 °C. Above 800 °C Au atoms leave the surface. If the surface temperature is much below 600 °C, small patches of (5 × 2) reconstruction form due to a low Au mobility.

In order to address the physics underlying the coalescence of (5 × 2) stripes, as a first step we would like to find out how the (5 × 2) terraces distribute on the surface. Unfortunately the STM system we worked on had a limited scan range which prevented us from obtaining large-scale images. Atomic force microscopy (AFM) seemed to be a good candidate giving its ability of acquiring micrometer-size images. Compared to STM, this range advantage comes at the cost of sacrificing the vertical resolution, i.e., in AFM images we could not distinguish (5 × 2) terraces from (7 × 7) terraces. To overcome this shortcoming, we deposited Co atoms onto a surface where most terraces had either (5 × 2) or (7 × 7) structure. The Co deposition allowed the formation of $CoSi_2$ islands on (5 × 2) terraces only, i.e., no islands formed on the (7 × 7) terraces. Instead, the (7 × 7) terraces transformed into $\left(\sqrt{7}\times\sqrt{7}\right)$ terraces for Co coverages less than ~0.2ML. [23] This effect is illustrated schematically in Fig. 3(a).

Fig. 3(b) is an AFM image showing a surface prepared by depositing 0.1ML of Au at 700 °C followed by depositing 0.1ML of Co at room temperature and annealed at 650 °C for 5 min. We can easily identify the (5 × 2) terraces through the presence of $CoSi_2$ islands. By taking many similar AFM images we were able to plot the distance distribution between neighboring (5 × 2) terraces, as shown in Fig. 3(c). The blue dotted curve is a fit to a Gaussian, indicating the existence of an optimal distance between two (5 × 2) terraces, which is ~200 nm. In the 0.2ML Au coverage experiment shown in Fig. 2 we have an optimal distance of ~170 nm. Thus the optimal distance can be preselected by depositing a suitable amount of Au.

Our images show that complete, uninterrupted (5 × 2) terraces are limited to the μm range. This limitation appears to come from two factors: the slight misalignment in the azimuthal angle of the surface, as shown in Fig. 1(b) where kinks appear at two steps, and the presence of domain boundaries in a terrace introduced by defects/vacancies. We estimate a misalignment of no more than 3° in the azimuth for the surfaces used here.

We now turn our attention to the physics governing the optimal distance. The domain formation energy per unit area E includes three terms:

$$E = E_r + E_b + E_{int}. \quad (1)$$

In Eq. (1), E_r is the energy needed per unit area to form a reconstructed surface from a bulk-terminated surface, E_b is the energy cost per unit area to form domain boundaries, and E_{int} is the interaction energy per unit area between elastic and/or electrostatic monopoles at the domain/terrace boundaries. [15,24] Since a transition from a structure of terraces with (5 × 2) stripes, as shown in Fig. 1(a), to a structure consisting of complete (5 × 2) and (7 × 7) terraces, as shown in Fig. 1(c), involves no change in E_r, i.e., the total (5 × 2) area is conserved, the energy difference between the two structures would come from changes in E_b and E_e.

For the experiment we have intentionally chosen a surface which has a miscut angle of 0.3° toward the [-211] direction. This particular surface provides an average terrace of ~60 nm wide, large enough to prevent step bunching. [18]. Consequently the step edges would stay put after Au deposition and subsequent heating. Another type of domain boundary is the intersection of the (5 × 2) stripe and the (7 × 7) structure within a terrace. This intersection moves as the surface is heated. Since the experiment was performed between 600 and 700 °C and this type of domain boundary moves freely, the energy associated with this type of domain boundary is small compared to the thermal