Coverage-Dependent Cobalt Structure on $\sqrt{3} \times \sqrt{3}$-Ag/Ge(111) Surface*

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By using STM, the surface structures of different cobalt coverage grown on $\sqrt{3} \times \sqrt{3}$-Ag/Ge(111) surface are investigated. We found that two kinds of structures appear on the cobalt films, one is $13 \times 13$ named Structure I, and the other is $2 \times 2$ named Structure II. Structure I is the structure of the islands with the height under 2 atomic levels, whereas the islands with other heights are Structure II. When the coverage of Co was increased, the transformation of structures reveals a two-stage evolution. The percentage of the Structure II increases rapidly at the coverage of about 1ML and 3 ML. However, the methods for these two elevations are different. The first stage of increasing results from sufficiency of cobalt atoms to form Structure II islands, but the second stage is due to the limitation of cobalt covered areas. The cobalt covered areas reach the limitation of 50% at the coverage of 3.5 ML. Moreover, for the cobalt island of 3.7 nm height, the configuration on the top still exhibits Structure II.

This result manifests that large amount of cobalt atoms do not transform into its bulk structure, instead, those cobalt atoms maintain the same structure with the bottom 2 x 2 layers. This coverage-dependent substitution of structures indicates that the transformation of cobalt islands is not due to phase transition. Besides, the exchange between cobalt atoms and the bottom silver layer can also be denied.

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I. INTRODUCTION

The developments of semiconductor industry encourage the interests of semiconductor-based devices for scientists. Nowadays growing metallic films on semiconductors receives great attention because of the Schottky Barrier at the interface. The Schottky barrier can make a sharp interface between the metallic films and the semiconductor substrates, and also enhance some specific phenomena [1, 2]. Furthermore, it is fascinating to grow magnetic thin metal films on semiconductors since it may be employed to design spin-based electronic devices [3, 4]. Magnetic nanometer-scale clusters also have high potential for application [5, 6]. Cobalt is one of the materials with high magnetization at room temperature. Germanium surface possesses better semiconducting property than silicon surface [7]. Investigating a system with these two materials can be a proactive idea.

In our previous study, the formation of Co adsorbed on $\sqrt{3} \times \sqrt{3}$-Ag/Ge(111) surface were reported [8, 9]. Two kinds of structural islands are found on the surface, Structure I is $13 \times 13$ R14° and Structure II is $2 \times 2$. Structure I is for Co islands less than two atomic layers while the Structure II is for Co islands of other heights. Besides, the structure transformation with different annealing temperatures for low Co coverage is also investigated. At 0.35 ML Co coverage, an intense structure transformation for Co islands occurred after 400°C annealing temperature because of the giant ascending motion. In this paper, the annealing temperature was fixed at 400°C but the influence of Co coverage was concerned. It can be considered as an advanced investigation.

II. EXPERIMENTAL

All experiments were carried out in an ultra-high-vacuum chamber with a base pressure less than $5 \times 10^{-11}$ Torr. The chamber was also equipped with a variable temperature scanning tunneling microscopy (VT-STM) and two well-collimated e-beam evaporators for depositing high purity Ag and Co atoms. A p-type Ge(111) substrate was cleaned by repeated cycles of ion bombardment (0.7 keV, Ar+) and annealing up to 800°C for ten hours, then slowly cooling down with a rate of 2°C per minute to room temperature. Ag atoms were deposited after clean Ge(111)-c(2 x 8) surface was shown. After depositing one monolayer (ML) of Ag and annealing to 500°C, the $\sqrt{3} \times \sqrt{3}$-Ag/Ge(111) surface was formed. Co atoms were deposited onto the clean $\sqrt{3} \times \sqrt{3}$-Ag/Ge(111) surface precisely at a rate of 0.01 ML/min. Each annealing treatment was performed by a resistance heater below the sample for an hour to make a thermal equilibrium surface. In addition, a K-type thermocouple for full range temperature was placed on the sample manipulator to measure the temperature of the sample.

III. RESULTS AND DISCUSSIONS

Figure 1 shows STM images of two kinds of Co islands in both negative and positive sample bias. Figures 1(a) and (c) are those of negative sample bias while (b) and (d) indicate those of positive sample bias. By comparing Figs. 1(a) and (b), it is obvious that the STM images of Co islands with Structures I are quite different. This difference is caused from variance in the electronic structure and also a general phenomenon for adsorbates on semiconductor surface [10–12]. In our previous study, Structure I is for the Co islands which are lower than two atomic layer [9]. Besides, the centers of trimers (both Ge trimers and Ag trimers) in $\sqrt{3} \times \sqrt{3}$-Ag/Ge(111) surface

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are the preferred sites for Co atoms. Although Co atoms do not form any compounds with the substrate, but the interaction between the lower-layer Co atoms and the substrate cannot be neglected. Therefore, the local density of states for Co atoms at different sites in the first two layer Co atoms can be affected by the substrate and behave as a semiconducting surface [10–12]. However, after the third layer of Co atoms was covered on the islands, the influence from substrate was reduced. The images in Figs. 1(c) and (d) indicate that the Co islands with Structure II show no difference between +1.9 V and 1.9 V. This phenomenon is similar to metal surface which lacks for bias contrast. Besides, Structure II is also more compact than Structure I. Thus these higher layers are more possible to have magnetic properties [13].

Figure 2 shows the coverage dependent structure transformation. First, it is easy to distinguish the difference between Figs. 2(a) and (b). Figure 2(a) is the STM image taken at 0.35ML Co coverage after 400°C annealing temperature. There are many Structure I islands (those darker islands) on the surface but only few Structure II islands (those brighter islands) are found. With numeric statistics for large area, it appears that there are only 18% of Co islands within Structure II at the coverage of 0.35 ML. However, while the coverage was increased to 1.4 ML, the percentage of Structure II was also increased rapidly to 80%. Structure II islands seized most part of Co covered area as shown in Fig. 2(b). More data are presented in Fig. 2(c). The percentage of Structure I and Structure II are drawn as a function of Co coverage. Note the percentage here is defined as the ratio of structure for total islands. The first elevation for 2×2 structure is due to the amount of Co atoms in a local area. At 0.35 ML, because the Co atoms are separated by a long distance, it is difficult to form Structure II islands. Since Structure II islands are more...
compact than Structure I islands, forming Structure I islands is easier for less Co atoms in a local area. When the coverage is more than 1.4 ML, the amount of Co atoms is quite enough to form Structure II islands. Therefore the percentage of Structure II Co islands increases intensely. Form 1.4 ML to 2.8 ML, the ratio of two structures seems to be invariable. However, the second elevation happened at 3.5 ML because of the saturation of Co covered area. As it shows in Fig. 3, the Co covered area approaches its saturation at the coverage of 3.5 ML. The saturated covered area is about 50% of the total area and at least 50% of the surface area remains Ag. The insert figure in Figure 3 is the STM image of 4.9 ML Co coverage and there appear many uncovered areas which exposed with substrate. The origin of this phenomenon is for reducing the surface free energy. The surface free energy of the silver surface is smaller than the surface free energy of the cobalt surface \((\gamma_{Ag} = 1.30 \text{ J/m}^2; \gamma_{Co} = 2.71 \text{ J/m}^2)\) [14, 15]. Likewise, for Co on Ag/Pt(111) surface [16, 17], the exchange behavior happens between Ag layers and Co layers. It means Co atoms tend to diffuse into Ag layers for exposing more Ag areas. More Ag layers on the surface exhibit less surface free energy. Nevertheless, since the binding between Ag and Ge atoms for \(\sqrt{3} \times \sqrt{3}\)-Ag/Ge(111) system [18] is far greater than the binding between Ag and Pt, the exchange behavior cannot demonstrate for Co atoms on Ag/Ge(111) surface. Instead, Co atoms start its ascending motion [19–21] to grow higher islands and minimize the surface free energy. This behavior leads to a consequence of the second evolution in structure. After 3.5 ML, the ratio of two structures keeps the same up to 4.9 ML and large percentage of Structure II islands were found on the surface.

Now we realize that the island transformation is related to the variation of Co coverage. This is helpful to clarify the problem before. In our previous study, we only investigated the structure transformation with annealing temperature [8]. It is difficult to confirm that whether the transformation is caused by phase transition. However, with these new evidences, the statement of phase transition can be demolished in this system. The structure transformation is just a result from the growing of island heights. Since Structure II is the structure for higher islands (\(>2\) atomic layers), it appears more Structure II islands when all islands grow higher and higher. Comparing to our former result [8], the structure transformation require high annealing temperature (\(\sim 500^\circ\text{C}\)) since the ascending motion needs more kinetic energy to overcome the barrier. However, for the annealing temperature below 500°C, the structure transformation can be dominated by the Co coverage because of a large difference in surface free energy between Co and Ag. The Co islands prefer to grow its height and contribute more Structure II configuration.

In our experiment, the structure of Co islands transformed from \(\sqrt{13} \times \sqrt{13}\ R14^\circ\) to \(2 \times 2\) at the third layer. It is interesting that how thick can the \(2 \times 2\) structure extend. Figure 4(a) shows a STM image of a Co island with 3.7 nm high. This is an isolated island which means that it is surrounded with no other islands. Hence the height of the island can be observed very clearly. The insert figure in Fig. 4(a) illustrates the line profile of the island and Fig. 4(b) is the enlarged image of the Co island. In Fig. 4(b), it is found that the structure on the top of island is still \(2 \times 2\). Even though the structure on the island is not very clear, but comparing with the insert figure which is taken from a lower Co island in the same scale, it is indeed \(2 \times 2\). Note the inner layer spacing between \(2 \times 2\) layers is only 0.2 nm. Therefore, it is surprising that the island with 3.7 nm high can still reveal in \(2 \times 2\) structure. This result implies that the \(2 \times 2\) structure is a stable structure and can be extended up to this height. We discreetly checked the structure on the island since the structure is similar to \(1 \times 1\) period. Although the structure of Co islands becomes metallic in higher layers, it still loathes returning to its bulk structure. This is perhaps due to the residual interaction between Co layers and the substrate, even though the interaction is not as strong as the first two layers. Otherwise it can be attributed to large stress for forming \(1 \times 1\) structure on Co islands.

In contrast, Structure I is \(\sqrt{13} \times \sqrt{13}\ R14^\circ\) which only appears in the first two layers. It is not a general con-
figuration, but it was found in both the cases of C$_{60}$ on Ge(111) surface [22] and polar SrTiO$_3$(111) surface [23]. Structure II is 2 × 2 and also not a bulk structure of Co. However it can be extended up to 3.7 nm high. Besides, the structure transformation can depend on the annealing temperature or the Co coverage. Yet the correlation is a little bit different, although the percentage of Structure II increases with both of them. The structure transformation is a continuous variation with annealing temperature while it becomes discontinuous with Co coverage. The reason is that there are some additional factors which were mentioned in the previous paragraph, contributing to the growth behavior.

IV. CONCLUSIONS

In summary, the coverage-dependent structure transformation of Co islands on $\sqrt{3} \times \sqrt{3}$-Ag/Ge(111) surface has been investigated. The transformation exhibits two-stage evolution. The first stage arriving at 80% of Structure II islands can be attributed to the vertical growth of Co islands. The ratio between Structure I and Structure II keeps the same up to 3.5 ML. After 3.5 ML the saturation of Co covered area cause the second stage evolution which exceeds 95% of Structure II islands and this percentage can maintain up to 4.9 ML. In addition, the metallic electronic structure and the extension in vertical epitaxy of Structure II islands make themselves possess magnetic properties. This fundamental growth behavior of magnetic island on semiconductor substrates can also be applied to help the developments of spintronic devices.

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