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Atomic structure of thin dysprosium-silicide layers on Si(111)

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Abstract

We report on scanning tunneling microscopy results of thin dysprosium-silicide layers formed on Si(111). In the submonolayer regime, both a $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ and a 5×2 superstructure were found. Based on images taken at different tunneling conditions, a structure model could be developed for the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ superstructure. For one monolayer, a 1×1 superstructure based on hexagonal DySi₂ was observed, while several monolayers thick films are characterized by a $\sqrt{3} \times \sqrt{3} R30^{\circ}$ superstructure from Dy₃Si₅. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Silicides of the trivalent rare earth metals grown as thin films on silicon surfaces are currently of high interest because of their low Schottky-barrier heights on n-type substrates [1-5], their epitaxial growth on Si(111) [6–18] and the self-organized formation of nanowires on Si(001) [19–23]. These silicide films can be prepared by rare-earth deposition and subsequent annealing. In several publications, the atomic structure of films on Si(111) has been studied using scanning tunneling microscopy (STM), showing a variety of structures mainly depending on the rareearth element and its coverage. Most of these studies were related to erbium silicides. The detailed atomic structure of the different structures occurring for dysprosium-silicide films on Si(111), however, is not completely understood up to now.

Here we present detailed scanning tunneling microscopy results on the growth of dysprosium-silicide films in the range from submonolayer coverages up to a few monolayers. Submonolayer silicide layers are characterized by domains of $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ and 5×2 superstructures. At one monolayer, a 1×1 structure is found, and several monolayers thick films form a $\sqrt{3} \times \sqrt{3} R30^{\circ}$ superstructure. Using a variety of tunneling conditions, we were able to derive the atomic structure of the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ submonolayer and the $\sqrt{3} \times \sqrt{3} R30^{\circ}$ multilayer films.

2. Experimental

 $Si(111)7 \times 7$ substrates were prepared by repeated flashing of n-type Si(111) wafers followed by slow cooling down in order to enable the formation of a defect-free reconstruction. The silicide films were grown in situ by depositing dysprosium on the clean Si(111)7 \times 7 surface held at room temperature, and afterwards annealing at 500 °C for 1 min to form the silicide. The base pressure was lower than 5×10^{-11} mbar and did not exceed 2×10^{-10} mbar during preparation. Such vacuum conditions are prerequisite for studying lanthanide silicides in order to prevent oxidation. Dysprosium exposures were determined using a quartz-crystal microbalance with an absolute accuracy of $\pm 20\%$. One monolayer dysprosium, defined using the density of silicon atoms at the unreconstructed Si(111) surface, corresponds to a dysprosium exposure of 2.5 Å. Annealing temperatures were controlled by an infrared pyrometer with an accuracy of about ± 20 °C. The STM experiments were performed using a non-commercial instrument. The tunneling tips were

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prepared by electrochemical etching of tungsten wires [24] and subsequent annealing in ultra-high vacuum.

3. Results and discussion

3.1. The general growth behavior

Representative overview images of the typical silicide structures are presented in Fig. 1. At submonolayer coverages (Fig. 1(a)), the surface is covered by domains of the bare Si(111)7×7 and occasionally also the Si(111)5×5 surface [25] as well as by thin silicide films with $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ and 5×2 superstructures. The $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ superstructure is characterized by triangular domains separated by linear dislocations. At sufficiently high coverages, also the rather flat monolayer structure becomes visible, which is shown in a detailed analysis to be characterized by a 1×1 reconstruction.



Fig. 1. STM overview images of the different types of dysprosium-silicide thin film structures (a) at a submonolayer coverage of 1.5 Å and (b) at a coverages of 7 Å corresponding to a few monolayers.

At coverages exceeding one monolayer (Fig. 1(b)), the substrate surface is not visible any more, and two differently shaped flat terrace structures appear. As will be demonstrated further below, these terraces are related to the 1×1 -reconstructed DySi₂ monolayer, which is characterized by linear terrace edges pointing in $[10\bar{1}]$ direction, and a multilayer film with a $\sqrt{3} \times \sqrt{3} R30^{\circ}$ superstructure and rounder terrace edges consisting of Dy₃Si₅.

3.2. The $2\sqrt{3} \times 2\sqrt{3}$ R30° superstructure

Detailed images of the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ superstructure taken at different polarities of the tunneling voltage are shown in Fig. 2. This silicide structure is formed exclusively at coverages up to 0.2 Å dysprosium, is dominant at half a monolayer, and can be observed at higher coverages up to



Fig. 2. STM images of the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ submonolayer structure at sample voltages (a) of +0.6 V and (b) of -1.4 V. The $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ unit cell is indicated.

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almost one monolayer. The size and orientation of the surface unit cell can be determined by direct comparison with that of the neighboring Si(111)7 × 7 surface. The structure is characterized by about 50 Å wide domains separated by linear dislocations aligned in $[11\overline{2}]$ direction, which are forming a triangular network. From a closer inspection of the structure it is found that the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ unit cell rotates by 60° at the dislocations.

The general appearance of this submonolayer structure is found to depend strongly on the tunneling polarity. At positive sample voltages, ring-like structures are observed in the image (Fig. 2(a)). In this case, the empty states are imaged, which are more related to dysprosium atoms because of their lower electronegativity as compared with silicon atoms. At negative sample voltages, the occupied states are imaged, which are hence mostly associated with silicon atoms. Here the images are characterized by windmill-like structures (Fig. 2(b)).

In the following, a structure model of the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ superstructure and its dislocation network will be presented. It is based on a direct comparison of images of the same surface area taken at different tunneling polarities, where the presence of the dislocation lines allowed determining the correct alignment of the observed features in both images. In this way it was found that the unit cells displayed in Fig. 2(a) and (b) coincide, enabling to derive the relative alignment of the dysprosium and silicon atoms. In particular it turns out that the dysprosium-related ringlike features do not coincide in position with the windmilllike features from the silicon atoms.

Since the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ structure is predominantly observed at coverages around 0.5 monolayers, it can be assumed that six dysprosium atoms contribute to every unit cell. Furthermore it has to be taken into account that a saturation of the dangling bonds of the substrate is required to minimize the energy. This means for the present case that all twelve dangling bonds of the unreconstructed Si(111) surface in the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ unit cell should be saturated.

The resulting structure model, as shown in Fig. 3, is based on hexagons consisting of six dysprosium atoms adsorbed at the unreconstructed Si(111) surface, similar to the case of the erbium-induced $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ superstructure [14,16]. In this way, each of the twelve silicon dangling bonds in the unit cell can bond to dysprosium atoms, so that every dysprosium atom saturates two silicon dangling bonds. Therefore the remaining third electrons of the generally trivalent dysprosium atoms are assumed to form a benzene-like hybrid orbital, as indicated by the orange hexagon in Fig. 3(b). Such an electronic configuration is assumed to stabilize the ring-like structure [16].

Among the 12 surface silicon atoms, six atoms are bonding to two dysprosium atoms, while the other six atoms only have one dysprosium atom in the close neighborhood. In particular the region in between two dysprosium hexagons is characterized by two silicon atoms with only one neighboring dysprosium atom and one with two dyspro-



Fig. 3. Atomic structure model of the submonolayer film with the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ superstructure within the dislocation network (a) overlaid on the filled-state image and (b) together with the substrate structure.

sium neighbors. This gives rise to an asymmetric bonding configuration of the silicon atoms, as shown by the filled blue arrows in Fig. 3(b),¹ which indeed matches well the observations in the filled-state image (Fig. 3(a)) when inspecting the position and shape of the single protrusions from the windmill-like features.

In this way, also the other features observed in the filledstates images can be explained: the windmill-like appearance with a rotational direction of the three protrusions can now be associated with the tangential alignment of the blue arrows indicating the bonding asymmetry within one windmill. Also the observation of deep holes in the corners of the unit cell and in the center of the windmills can be related to triple silicon atoms, each of them having only

 $^{^{1}}$ For interpretation of color in Figs. 3, 6 and 7 the reader is referred to the web version of this article.

one dysprosium neighbor. In contrast, the faint protrusions in the centers of the dysprosium hexagons stem from triple silicon atoms, each of them having two dysprosium neighbors.

It should be noted that the symmetry of this structure model should in principle also allow windmill positions rotated by 60° around the center of the dysprosium hexagon. However, the filled-state images clearly show three windmills surrounding each dysprosium hexagon. Since the positions of the three windmills relative to the surrounded dysprosium hexagon rotates by 60° when crossing a dislocation line, a tip-related artifact can be excluded. Thus it has to be assumed that a further polarization of the asymmetric bonding configurations with a radial shift towards the center of the windmill occurs, resulting in the observed images.

The structure model and the assignment of the observed features are further supported when inspecting the dislocation lines and their intersection nodes in Fig. 2. At positive sample bias, the dislocation lines show a meander-like structure, while they appear at negative bias in form of slightly undulating lines with a considerably lower tip height than the windmill-like features. This behavior nicely agrees with a meander-like arrangement of the dysprosium atoms on top of the unreconstructed silicon surface, as indicated by the green meander line in Fig. 3(b). Such a



Fig. 4. STM images of the 5×2 submonolayer structure at sample voltages (a) of ± 1.4 V and (b) of ± 1.4 V. The 5×2 unit cell is indicated.

dysprosium structure results in an alternating chain of asymmetric bonding configurations of the silicon atoms, as marked by the open blue arrows, and therewith in the slight undulation observed in the filled-state image. These bonding configurations are structurally different from those responsible for the windmill-like features, since only



Fig. 5. STM images of the surface structure at (a) 1.2 Å, (b) 2 Å, (c) 3 Å, and (d) 5 Å dysprosium exposure.

one silicon atom bonding to one dysprosium atom is involved, explaining the observed difference in contrast.

Using the same arguments, the intersection nodes of the dislocation lines can be attributed to one dysprosium hexagon, marked in green in Fig. 3(b), where six meander lines are starting in non-radial directions. However, the different bonding configuration at the node with all silicon atoms bonding to two dysprosium atoms results in an electronic configuration with an average of only 3/2 electrons of every dysprosium atom necessary to saturate the silicon dangling bonds. In this way, 3/2 electrons remain at every dysprosium atom making the structure more instable, as indeed frequently observed in form of defective intersection nodes.

3.3. The 5×2 superstructure

At coverages above 0.3 Å dysprosium, also the 5×2 -reconstructed submonolayer structure becomes visible and dominates as compared with the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ structure at coverages close to one monolayer. Detailed scanning tunneling microscopy results are shown in Fig. 4. The appearance of this chain-like structure in $[10\overline{1}]$ direction also varies considerably when changing the tunneling polarity. However, a closer analysis of this structure and the development of a structure model is presently not feasible because of the much smaller available data basis and possible tip-shape related artifacts in the images in Fig. 4.

3.4. The 1×1 superstructure

In Fig. 5, the development of the surface appearance as a function of coverage is shown. Already at half a monolayer dysprosium, characteristic flat terraces with straight edges in the $[10\overline{1}]$ direction of the silicon substrate are observed, which are related to the silicide monolayer. This behavior indicates a significant lateral diffusion of dysprosium atoms during silicide formation. The terraces dominate around one monolayer corresponding to a dysprosium exposure of 2.5 Å. As will be shown in the following, these terraces have a 1×1 unit cell and consist of a monolayer of hexagonal DySi₂. At coverages exceeding one monolayer, terraces with rounder edges become dominant, which show a $\sqrt{3} \times \sqrt{3} R30^{\circ}$ superstructure characteristic of hexagonal Dy₃Si₅.

In order to derive the atomic structure of these terraces, rather extreme tunneling conditions with high tunneling currents up to 7 nA and low tunneling voltages around 0.3 V had to be chosen. In this way, the tunneling images showed sufficient corrugation.

In Fig. 6^1 such high-resolution images are shown for the silicide monolayer together with a structure model. This structure is already known to consist of a surface with buckled silicon hexagons, while the dysprosium atoms are found underneath the surface [10]. In this way, the images mainly show the dangling bonds of the uppermost silicon atoms. At positive sample bias (Fig. 6(a)), also the electronic states



Fig. 6. STM images of the 1×1 monolayer structure at sample voltages and tunneling currents (a) of +0.3 V and 7 nA and (b) of -0.3 V and 3 nA. The 1×1 unit cell is overlaid. (c) and (d) show the structure model of the DySi₂ monolayer.

from the silicon atoms in the lower surface layer are observed, so that the complete structure of the surface bilayer with its buckled hexagons [10] becomes visible.

The observed edges in $[10\overline{1}]$ direction are in nice agreement with the structure model, since the density of silicon dangling bonds is minimum for this edge orientation. Similar observations were already made for the case of erbiumsilicide monolayers [11-13].

3.5. The $\sqrt{3} \times \sqrt{3} R30^\circ$ superstructure

In Fig. 5(d) a multilayer dysprosium-silicide film is shown, where the number of layers is marked. While the terraces of the $DySi_2$ monolayer (marked 1) still show very straight edges in the $[10\overline{1}]$ direction of the substrate and sharp corners, the Dy_3Si_5 double layer (2) is already characterized by softer corners, although the edges are still pre-



Fig. 7. (a) STM filled state image of the $\sqrt{3} \times \sqrt{3} R30^{\circ}$ multilayer structure at sample voltage and tunneling current of -0.3 V and 4 nA. The $\sqrt{3} \times \sqrt{3} R30^{\circ}$ unit cell is overlaid. (b) and (c) show the structure model of the Dy₃Si₅ multilayer in top view and side view, respectively.

dominantly aligned in $[10\overline{1}]$ direction. The triple layer (3) has more or less arbitrarily formed edges without any specific orientation.

Fig. 7(a)¹ shows high-resolution data of the multilayer structure. This structure is known to have a surface consisting of buckled silicon hexagons, while the silicon hexagon layers underneath are planar with every sixth silicon atom missing, giving rise to the $\sqrt{3} \times \sqrt{3} R30^{\circ}$ superstructure [8,17,18]. These vacancies in the second silicon layer have a strong influence on the tunneling probability, resulting in the observation of bright triangles with triple protrusions and dark holes in between.

A detailed analysis of the microscopy results leads to a structure model shown in Fig. 7(b) and (c). The only feature in the image with the $\sqrt{3} \times \sqrt{3} R 30^\circ$ periodicity and the threefold symmetry of the silicon vacancies is the center of the bright triangle, which is thus representing the position of the vacancy. It is interesting to note that the vacancies are located underneath the lower silicon surface atom. This behavior, observed here for thin Dy₃Si₅ films, is similar to observations at thick Er₃Si₅ films [15], but in contrast to thin Er₃Si₅ films where the vacancies were found underneath the top silicon surface atoms [13]. Thus the atomic structure of thin Dy₃Si₅ and Er₃Si₅ films is found to be slightly different.

The form of the terrace edges can again be related to the density of the silicon dangling bonds at the edges: Since bulk Dy_3Si_5 is characterized by an ordered arrangement of vacancies in the planar silicon layers [8], there is almost no anisotropy in the density of the dangling bonds produced during edge formation, in contrast to the buckled silicon layer at the surface of Dy_3Si_5 or $DySi_2$ that is free of vacancies. At thick Dy_3Si_5 layers, where the relative influence of the surface decreases, the terraces thus become rounder.

4. Summary

Using high-resolution scanning tunneling microscopy, we were able to observe different atomic structures during growth of dysprosium silicides on Si(111). At submonolayer coverages, structures with $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ and 5×2 periodicity were found. A detailed structure model could be derived for the $2\sqrt{3} \times 2\sqrt{3} R30^{\circ}$ superstructure as well as for the dislocation network separating the single-crystalline domains. The monolayer is formed from hexagonal DySi₂ with a 1×1 periodicity, and both silicon layers in the buckled silicon surface could be resolved. Finally, also the structure of thin multilayer Dy₃Si₅ films could be derived, which is characterized by a $\sqrt{3} \times \sqrt{3} R30^{\circ}$ superstructure induced by silicon vacancies in the silicide bulk.

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