Growth of Ultra-Thin MnSi Films on Si(111) Surface: Monte Carlo Simulation

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Thin MnSi films growing by units of a quadruple layer of a B20-type structure are observed on the Si(111) surface by scanning tunneling microscopy. Based on the observation, a model of growth controlled by an interplay between MnSi crystal growth and supply of Si atoms from substrate is proposed. A simple Monte Carlo model efficiently simulating significant experimentally observed features is presented. [DOI: 10.1380/ejssnt.2008.276]

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I. INTRODUCTION

MnSi flat films fabricated on the Si(111) surface have recently attracted attention as a promising material for spin-based electronic devices. According to ab-initio calculations [1], MnSi can exist in a form of a flat film with a B20-like structure. Importantly, these films exhibit 50% of spin polarization according to the calculation. In our preceding publication [2] we presented conditions leading to almost atomically flat MnSi films on the Si(111) surface. We have shown that room temperature (RT) deposition of ~ 3 monolayers (ML; 1 ML = 7.83 × 10^14 atoms/cm^2) and annealing to 250°C resulted in surface covered mostly by flat MnSi films with (√3 × √3)R30° reconstruction (hereafter called (√3 × √3) for simplicity). We also demonstrated that the film grows by units of quadruple layers (QL) of the B20 MnSi (see Fig. 1) and that 2 QLs are preferred against 1 QL during initial growth.

Understanding a rather complicated process of the MnSi film formation is crucial for further improvement of the film quality, which is essential in its utilization for spin-based devices. In the MnSi B20 structure, silicon and manganese atoms are equally included. Therefore, after deposition of some amount of Mn, the same amount of Si must be provided by the surface. A resulting morphology is thus by necessity influenced by MnSi crystal growth and by decomposition of Si layers.

For growth of thin films on oriented surfaces of crystals, kinetic Monte Carlo simulations are widely used [3] in order to test proposed models and provide a quantitative evaluation of physical parameters. However, simulations of such complicated systems as silicides are rather challenging, mainly because of too many processes involved during silicide formation and high number of related parameters.

Here we present a minimal model of MnSi growth based on our experimental results. The model is tested by a Monte Carlo simulation. We show that even with highly simplified model with just few parameters it is possible to explain all important experimentally observed features.

II. EXPERIMENTAL

MnSi films were grown on Si(111)7×7 surfaces by depositing Mn from a home-made Ta tube and subsequent annealing. Deposited amount was estimated by a quartz crystal thickness monitor. The Si(111)7×7 reconstruction was prepared by a standard flashing procedure and confirmed by the low-energy electron diffraction. Samples were annealed to 250°C for several minutes. Temperature was measured by infra-red pyrometers. Morphologies of the samples were observed by a UNISOKU scanning tunneling microscope (STM) at RT few hours after...
preparation. The base pressure of apparatus was about $1.0 \times 10^{-10}$ Torr.

III. RESULTS AND DISCUSSION

A. STM observation of film morphology

In this section we summarize experimental results of STM observation. For further details, see Ref. 2.

Fig. 2(a) shows a constant-current STM image of 1.5 ML Mn deposited sample. On the figure, MnSi islands (white and light gray) coexist with bare Si surface (dark gray). On closer inspection two levels of bare Si can be seen, e.g. in the area outlined by a rectangle. Magnified image of this area is shown in Fig. 2(d). Lower level of the Si surface (bottom part of the figure) shows a disordered structure, mostly with $2 \times 2$ periodicity, while the higher level (marked by an arrow) exhibits a partly broken $7 \times 7$ structure. Thus it can be deduced that the higher Si level is the original, partly survived $7 \times 7$ surface, while the lower level is area, where one bi-layer of Si was removed during growth of MnSi. A line profile extracted along the line indicated in Fig. 2(a) is plotted in Fig. 2(f). The profile crosses area of survived $7 \times 7$ (left part), areas of removed Si bi-layer (marked by “x”) and MnSi islands of two different heightes (indicated by hatching). A level of the original surface is marked by a dashed line. Difference of height of higher and lower MnSi island is $\sim 3$ Å, which is consistent with a growth by units of quadruple layers of B20-type structure (Fig. 1), as we previously reported [2]. From STM images, we measured area of two levels of MnSi, obtaining $\sim 20\%$ occupation of the higher and $\sim 30\%$ of the lower level. Recalling the density of Mn in a QL of B20 is 4/3 ML we can approximate amount of Mn in the islands. Using the thickness of the lower and higher level as 2 and 3 QLs we obtain amount of 1.6 ML, which is in a good agreement with the value measured by a crystal monitor. Therefore we propose that the lower level of MnSi is 2 QL thick and the higher one is 3 QLs. Levels in the Fig. 2(f) are marked correspondingly. Using a bulk lattice-plane distance between QLS in B20 structure (2.7 Å), a thickness of 2 QLs and 3 QLs is 5.4 Å and 8.1 Å, respectively. This suggests that the MnSi growth under the original level of $7 \times 7$, i.e. one bi-layer of Si is removed on the site of MnSi growth and replaced by MnSi, as indicated by hatching in the Fig. 2(f). We note that a level of MnSi corresponding to a single QL is not observed on our STM figures.

Fig. 2(b) shows the sample after deposition of $\sim 3$ ML of Mn. The surface is almost completely covered by MnSi with $\sqrt{3} \times \sqrt{3}$ termination [unit of the $\sqrt{3} \times \sqrt{3}$ is outlined in a magnified image in Fig. 2(e)]. Next to the main flat area, few islands and tiny holes can be found on the surface. By considering deposited amount and occupation by the present levels of MnSi we obtained that the main level of MnSi is 2 QLS thick and the islands are 3 QLS. Plot profile along the line marked in the Fig. 2(b) is plotted in Fig. 2(g), demonstrating the flat area (marked “2”), island (marked “3”) and a hole. The surface after deposition of 5 ML of Mn is shown in Fig. 2(c). At this coverage the surface became rather corrugated with many levels of MnSi. Similar results were obtained previously [4]. A selected line profile extracted from the Fig. 2(c) is shown in the Fig. 2(h) with approximate thickness of the MnSi levels.

The observation can be summarized in few points: (1) MnSi grows by means of units consistent with quadruple layers of the B20 structure. (2) A minimum thickness of observed MnSi is 2 QLS. (3) Silicon necessary for formation of the MnSi film is provided by canceling bi-layers of Si both on site of MnSi and from surrounding area. (4) At about 3 ML of Mn the surface is almost completely covered by 2 QLS of MnSi. (5) At higher coverages the surface becomes corrugated.

B. Minimal model and Monte Carlo implementation

Based on the observation described in the previous section we propose a physical model of growth of MnSi. At elevated temperature, Mn atoms react with Si surface, partially destroying originally flat $7 \times 7$ surface. If a concentration of Mn is locally sufficient, MnSi is formed, 2 QLS are preferred to a single QL. When the surface becomes covered by a silicide film, another layers of MnSi are formed on top of the film, while Si atoms are supplied from holes in the film. Thus with increasing coverage over $\sim 3$ ML the surface becomes corrugated as many levels are formed and deep holes are created to supply Si atoms. Upon longer annealing, the less stable (isolated or edge) areas of MnSi decay and re-crystallize to a more stable formation.

Next we proceed to describe a minimal model sufficient for simulation of MnSi film formation and its Monte Carlo implementation. In our model, the surface is represented by separated matrices for MnSi and Si, the smallest (coarse-grained) unit is a triangular half of $\sqrt{3} \times \sqrt{3}$ unit cell (UC) with height of 1 QL in the case of MnSi and 1 bi-layer in the case of Si. Diffusion by single hopping of atoms between adjacent positions, as is common in a conventional kinetic Monte Carlo simulation of thin film growth, is not implemented in our simulation in order to keep the model the simplest possible and with minimum of parameters. Structures of MnSi and Si(111)=$7 \times 7$ surface are implemented only by means of concentration of Mn and Si atoms, i.e. one quadruple layer of MnSi consists of 4/3 ML of Mn and 4/3 ML of Si, one bi-layer with $7 \times 7$ reconstruction (original surface) consists of 2.08 ML and a bi-layer of Si of lower levels consists of 2.0 ML. In terms of unit cells, one MnSi UC contains 2 Si and 2 Mn atoms, one original-surface-silicon UC contains 3.12 Si atoms and one lower-level-silicon UC contains 3 Si atoms.

The simulation is divided to two stages. During the first stage, MnSi film is formed with supply of Si atoms by means of formation of holes. This stage is irreversible and corresponds to very initial reaction of Mn with Si surface upon annealing. Three general processes are considered in this stage.

1a) Formation of 2 MnSi UCs on bare Si surface implemented to mimic preferred growth of 2 QLS thick film. In this process, one Si UC is removed and two UCs of MnSi are formed on the site. For formation of 2 MnSi UCs, 4 atoms of Si are necessary. 3.12 Si atoms or 3 atoms are supplied by removing surface or lower UC of Si.
FIG. 2: STM images of MnSi thin films on Si(111) surface prepared by annealing to 250°C. (a) 1.5 ML Mn deposited sample. Brighter islands are MnSi films, darker gray is bare Si surface. (b) 3 ML Mn deposited sample. Most of area is covered by flat MnSi film, several islands and holes are observed. (c) 5 ML Mn deposited sample. Surface shows high corrugation, many levels of MnSi are observed together with deeper holes. (d,e) magnified image of area marked by rectangles in (a,b). Arrow in (d) points to a survived corner hole of the 7 × 7 reconstruction. In (e) a unit of (√3 × √3)R30° is outlined. (f-h) line profiles along lines marked in (a-c). Numbers denote a probable local thickness of the MnSi film. Size of images (a-c) is 60 × 60 nm², (d,e) are 10 × 10 nm².

1b) Formation of 1 MnSi UC on top of existing MnSi. The process is consuming 2 Si atoms from the reservoir of “free” Si atoms.

1c) Formation of hole in bare Si surface. 3.12 or 3 Si atoms are supplied to the reservoir of “free” Si atoms if the hole is formed on the original surface or on a lower level, respectively.

Each type of process is divided to four possibilities with respect to a number of the nearest neighbors. A simple linear bond-cutting model is used, so the relative probability of formation of hole (process 1c) on a site with n nearest neighbors is \( \exp(-n \times E_{Si}/kT) \), where \( E_{Si} \) is effective energy of bond between neighboring units of Si, \( k \) is the Boltzmann constant and \( T \) is the temperature. On the other hand, formation of MnSi (processes 1a and 1b) on highly coordinated sites is preferred and the relative probability is \( \exp(n \times E_{MnSi}/kT) \), where \( E_{MnSi} \) is an effective energy of bond between neighboring MnSi units. Here we note that attempt frequencies for all processes are considered equal in our simulation for simplicity. Different values of the frequencies can in fact effectively influence values of the activation energies.

Formation of MnSi during the first stage proceeds as follows: Initially, there are no “free” (not incorporated in UCs of MnSi or Si) Si atoms, which is used to control mass balance during the simulation, as we describe later.

2a) Removing one MnSi UC.
2b) Random formation of a new UC of MnSi.

Realization of the event 2a is again selected randomly with weight of \( \exp([-n \times E_{MnSi} + E_v]/kT) \) where \( n \) is number of the nearest horizontal neighbors, \( E_{MnSi} \) is the effective energy of bonding to the nearest neighbors and \( E_v \) is effective energy of bonding to an underlying MnSi.

The second stage corresponds to a recrystallization of MnSi during annealing. During this stage, amount of Mn on the surface is constant and matrix of Si surface is not changed. Two processes are repeated:

2a) Removing one MnSi UC.
2b) Random formation of a new UC of MnSi.
layer, different for Si to MnSi \( (E^v_{\text{MnSi-Si}}) \) and MnSi to MnSi \( (E^v_{\text{MnSi-MnSi}}) \) bonding. A position of re-appearing of new MnSi unit (event 2b) is selected randomly in order to effectively simulate diffusion of freed Mn and Si atoms. During the recrystallization stage, the MnSi film evolves in direction to minimum of total energy by means of preferring highly coordinated positions. Two parameters are to be fitted during this stage: \( E^v_{\text{MnSi}} \) and \( \Delta E^v = E^v_{\text{MnSi-MnSi}} - E^v_{\text{MnSi-Si}} \).

Results of simulation for 1.5 ML, 3 ML and 5 ML of Mn are shown in Fig. 3(a-c). The following values of the model parameters were used: \( E^v_{\text{Si}} = 0.31 \text{ eV}, E^v_{\text{MnSi}} = 0.07 \text{ eV}, P_{\text{Si/Mn}} = 5, E^v_{\text{MnSi}} = 0.4 \text{ eV} \) and \( \Delta E^v = 0.20 \text{ eV} \). Line profiles extracted along lines marked in (a-c) are shown in Fig. 3(d-f). All scales are set to be same as in Fig. 2(a-c), so that STM and Monte Carlo results can be directly compared. In the 1.5 ML case, the same levels of MnSi and Si can be observed on the simulated and STM images - 2 and 3 QLs of MnSi, an original Si surface and a lower Si surface. Compared to the experiment, occupation by level of 2 QLS (3 QLS) is higher (lower) in case of simulation. Possible reasons will be discussed later. In the 3 ML case, the agreement between experiment and theory is reasonable [Fig. 2(b) and Fig. 3(b)]. In both cases, the surface is mostly covered by 2 QLSs of MnSi, the rest are islands of 3 QLSs and small holes. Corrugation of the surface after 5 ML deposition is reproduced well by the simulation [Fig. 3(c)] as well. Same levels of 3, 4 and 5 QLSs are observed as in Fig. 2(c) together with very deep holes.

On the line profiles in Fig. 3(d-f), small steps up and down with height of 0.4 Å can be seen [see e.g. position marked by an asterisk in Fig. 3(d)]. Such a step is a result of a similar thickness of Si bi-layer (3.1 Å) and MnSi quadruple layer (2.7 Å). For example, two QLSs and one QL plus extra Si bi-layer have a thickness of 5.4 Å and 5.8 Å, respectively. On our STM images (not shown here), we have observed such slight and smooth corrugation suggesting that steps at Si-MnSi interface can be crystalically overgrown and the small difference in height (0.4 Å) can be overcome by means of MnSi crystal relaxation.

Finally we discuss impact of simplifications of the model and limits of its application. First simplification to be mentioned is excluding of atom-by-atom diffusion. On a real surface, free Si and Mn atoms diffuse on the surface, interacting together as well as with steps of Si and edges of MnSi. In our simulation, the diffusion is simplified to annihilation of MnSi UC and random reappearance of the whole unit with no correlation to a position of the original MnSi UC. Such effects like diffusion barriers along step edges may of course influence values of model parameters. Thus we emphasize that the model parameters are indeed just of effective values.

Another simplification is recrystallization restricted only to MnSi, while the Si crystal is not allowed to restructure during the second stage described above. Experimentally, evolution of Si step edges was studied by high-temperature STM [5-7]. For example, an Si island of \( \sim 100 \text{ nm} \) size almost decayed after 60 min at 560°C. Possibly, the decomposition of a step edge may be faster in the case of Mn deposited surface, because of a reaction with free Mn atoms. However, we suppose that our simplification is acceptable in the case of temperatures bellow \( \sim 500°C \).

The last simplification to be discussed is neglecting of a possible inhomogeneity of Mn atom density before crystallization starts. It has been proposed that to form the MnSi, Mn atoms need to cluster together and form clusters with a sufficient size to react with Si substrate [8, 9]. This effect is stronger in the case of low coverage and can result in a formation of higher islands. This may be the reason why the occupation by the level of 3 QLSs is higher on STM images (Fig. 2a), compared to the simulation (Fig. 3a).

IV. CONCLUSION

Based on STM observation of morphology of MnSi thin films grown at 250°C we proposed a model of the film formation. The film grows by units with thickness of a quadruple layer of B20 type structure. 2 QLSs are preferred during initial MnSi formation. Silicon atoms necessary for MnSi growth are provided both on site of the formation and from bare Si surface. We have tested the proposed model by a simple coarse-grained Monte Carlo simulation. Obtained results are in a good qualitative agreement with experimentally observed morphology.

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