

The mechanism for the high-quality single-phase growth of MnSi films on Si (111) in the presence of Sb flux

Y. Yan^{a)} and M. M. Al-Jassim

National Renewable Energy Laboratory, Golden, Colorado 80401

K. Matsuda, H. Tatsuoka, and H. Kuwabara

Faculty of Engineering, Shizuoka University, Hamamatsu 432-8561, Japan

S. J. Pennycook

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831

(Received 2 August 1999; accepted for publication 7 September 1999)

The microstructures of high-quality single-phase MnSi layers grown on Si (111) by Mn deposition and reaction with Si in the presence of Sb flux are characterized by Z-contrast imaging. It is found that there is a transition layer consisting of two Sb monolayers sandwiching a Mn layer in between the Si substrate and the single-phase MnSi film. This Sb–Mn–Sb sandwich layer effectively prevents deposited Mn atoms from direct reaction with Si atoms in the substrate to form Mn silicides. This explains why high-quality single-phase MnSi layers can be grown with remarkably smooth interface on Si (111) substrates. © 1999 American Institute of Physics.

[S0003-6951(99)01645-9]

Metal–silicide/silicon interfaces have drawn extensive attention because of their microelectronics applications.^{1,2} While many studies have been carried out on W, Ti, Co, and Ni silicides,^{3–5} much less attention has been paid to silicides of the group VIIA elements, such as Mn. It is reported that MnSi, a cubic FeS structure, shows a magnetic transition at $T_c = 29.1$ K from a paramagnetic state to a helicoidal order. Its interesting magnetic properties make it a promising material for use in electronic and optoelectronic devices.^{6–8} However, there are few reports to date on the growth of Mn-based layers on Si substrates. The main reason is due to the difficulties of growing a high-quality single-phase layer with a smooth interface. In the most common growth procedures, Mn atoms easily react with Si atoms in the substrate to form many different polycrystalline Mn–silicides phases, resulting in a very rough interface.^{9–12} Very recently, the growth of high-quality single-phase MnSi films on Si (111) has been reported with remarkably smooth interfaces.^{13,14} The critical factor for the growth is the presence of an Sb flux. Without the presence of Sb, polycrystalline Mn–silicides form leading to rough interfaces. Thus, understanding the effects of the Sb flux during the growth will enable the growth of higher-quality films. However, so far no conclusive mechanism has been given.

In this letter, we report our Z-contrast imaging studies on the interfaces of high-quality single-phase MnSi films grown on Si (111), which reveal the growth mechanism for high-quality films.

The MnSi films were grown on Si (111) substrates by hot-wall epitaxy. The substrates were solvent degreased, etched in HF solution, and rinsed with de-ionized water. The oxide layer was etched away by immersing the wafers in a dilute hydrofluoric acid solution (HF:H₂O = 1:10), and dried prior to loading into the vacuum chamber. Growth was per-

formed by simultaneous exposure of the Si substrates, held at a temperature of 350 °C, to Mn and Sb atoms. The Mn flux used was 2×10^{14} atom/cm²s, while the Sb/Mn flux ratio supplied to the Si surface was 10.

Specimens were prepared for electron microscopy by first mechanical polishing to ~ 100 μm , then dimpling the central portion of the specimens to ~ 5 μm . Samples were thinned to electron transparency using a 4 kV Ar ion beam at 14° inclination and then cleaned at lower voltage (1.5 kV). A liquid N₂ cooling stage was used in order to minimize the damage during the ion milling. The Z-contrast images were formed by scanning a 1.26 Å probe across a specimen and recording the transmitted high-angle scattering with an annular detector (inner angle ~ 45 mrad). The image intensity can be described accurately as a convolution between the electron probe and an object function. Thus, the Z-contrast image gives a directly interpretable, atomic resolution map of the columnar scattering cross section in which the resolution is limited by the size of the electron probe.^{15,16}

The quality and orientation of the Mn–Si film and the smoothness of the interface have been characterized by conventional transmission electron microscopy previously.^{13,14} The Mn–Si layer was confirmed to be the single MnSi phase, with the epitaxial relationship between the MnSi layer and the Si substrate given by (111), $[\bar{1}\bar{1}2]$ MnSi \parallel (111), $[\bar{1}\bar{1}0]$ Si. The MnSi/Si interface is remarkably smooth, as seen in the low magnification Z-contrast image of Fig. 1. The electron beam is parallel to the $[\bar{1}\bar{1}0]$ zone axis of the Si substrate. The MnSi layer gives higher intensity than the Si substrate because Mn atoms have a higher atomic number ($Z=25$) than Si ($Z=14$). It is seen that the interface is very smooth, consistent with previous results.

Figure 2(a) shows a higher-magnification Z-contrast image of the MnSi/Si interface viewed along the $[\bar{1}\bar{1}0]$ zone axis of Si. The lattice image of Si is clearly seen, in which the bright spots correspond to atomic columns. It is seen that

^{a)}Electronic mail: yyan@nrel.gov

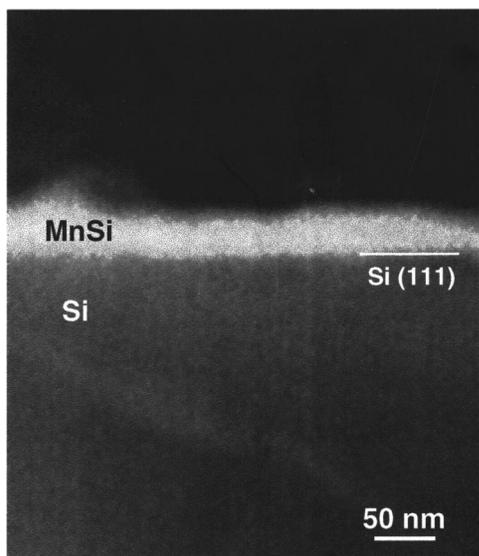


FIG. 1. Low-magnification Z-contrast image of an epitaxial MnSi film grown on Si(111) showing a very smooth interface.

the MnSi/Si interface is atomically smooth. It is surprising that the first two planes of the grown film are much brighter than either the Si or the MnSi layer. Figure 2(b) shows the intensity profile measured from the dotted box region across the interface. The position of the interface is indicated by an arrow. The two peaks at the interface have much higher intensities than bulk MnSi or Si. This strongly suggests that Sb atoms have segregated to the interface. This is consistent with SIMS measurements showing Sb segregation on the interface.¹⁷

Figure 3 is an enlargement of the image showing details of the structure of the interface. The Si dumbbells (pairs of atomic columns with a separation of 0.136 nm) are clearly

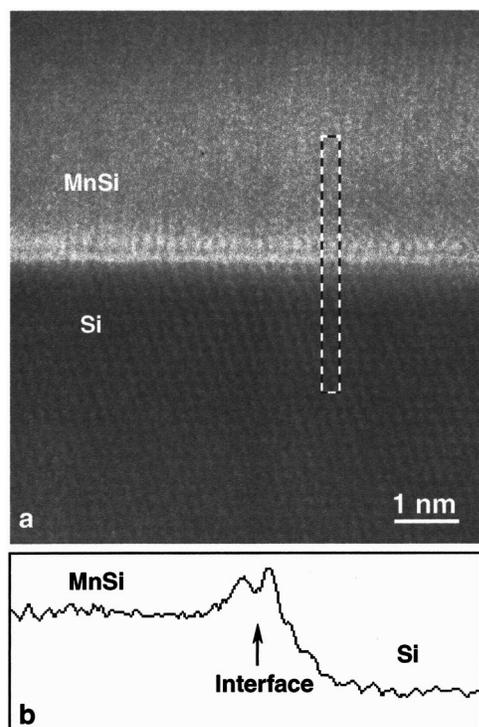


FIG. 2. Higher-resolution Z-contrast image of the MnSi/Si interface showing a narrow band of Sb segregation at the interface.

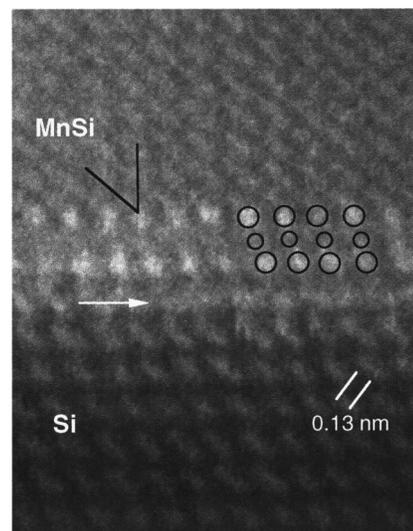


FIG. 3. High-resolution Z-contrast image of the MnSi/Si interface showing the Sb-Mn-Sb sandwich structure at the interface.

visible. Also seen is a monolayer of Sb atoms bound to Si atoms on the (111) surface of the substrate (indicated by larger circles). The separation of two adjacent Sb columns is the same as that of two adjacent dumbbells. The first monolayer of Sb modifies the surface of the substrate: the Si columns at the surface no longer have the dumbbell shape as indicated by the white arrow. The small increase of intensities for some Si columns at the surface suggests a small occupation of Sb in those columns. Above the first monolayer of Sb is another monolayer as indicated by smaller circles. The intensities of columns in this layer are higher than Si columns in the substrate but lower than Sb columns, indicating that they are Mn columns. This layer of Mn is sandwiched by two Sb monolayers. The MnSi film then grows epitaxially on top of the second Sb monolayer. The two dark lines show how two planes of MnSi match the Sb-Mn-Sb structure.

It has been reported that Sb-Si adsorption can easily occur on Si surfaces even at low temperature.¹⁸ The desorption of Sb on Si (111), i.e., the breaking of Sb-Si bonds, takes place only above a peak temperature of $T_p = 950^\circ\text{C}$. This indicates that the Sb-Si bonds on the Si (111) surface are energetically very stable. Since the Sb/Mn flux ratio supplied to the Si surface was 10, it would greatly enhance the formation of Sb-Si bonding. The substrate temperature (350°C) is too low to break the Sb-Si bonds. Thus, a monolayer of Sb can easily form and firmly cover the Si (111) surface. However, it is known that the free energy of formation of MnSi (7.25 kcal/g atom) is significantly higher than that of MnSb (3.25 kcal/g atom).¹⁹ Thus, the formation of MnSi is thermodynamically favored as compared with MnSb. A thick layer of MnSb is therefore not expected at the interface. This is consistent with the fact that only a Sb-Mn-Sb sandwich layer is observed at the interface.

It is believed that reaction between deposited Mn and Si in the substrate is responsible for the formation of many different polycrystalline Mn-silicide phases that lead to rough, wavy interfaces. The growth mechanism for the high-quality MnSi films on Si (111) in the presence of Sb flux has not so far been understood. However, it is now seen from the

above observations, that in the presence of the Sb flux, a Sb–Mn–Sb sandwich structure forms and covers the surface prior to growth of the MnSi film. This Sb–Mn–Sb structure prevents the diffusion of Mn into the substrate to react with Si and form Mn silicides. This forces the epitaxial growth of the single MnSi phase with an atomically smooth interface. Thus, it is clear that the mechanism for the growth of high-quality single-phase MnSi film with a smooth interface is the formation of the Sb–Mn–Sb sandwich structure as a result of the presence of Sb flux during the growth. This is very similar to the recent report on the growth of Ge on Si:^{20,21} With the presence of Sb as a surfactant, the inner diffusion of epitaxial Ge atoms into the Si substrate is greatly suppressed, leading to the formation of a very abrupt Ge/Si interface. In both cases, excess surfactant floats on the surface of the growing film. In our case, however, some is used to form the Sb–Mn–Sb sandwich structure at the film/substrate interface.

In conclusion, we have studied the structure of high-quality smooth MnSi/Si interface using Z-contrast imaging. We found that the formation of a Sb–Mn–Sb sandwich layer on the Si (111) surface is the reason that high-quality single-phase MnSi films can be grown with atomically smooth interfaces.

The work at NREL was supported by the U.S. Department of Energy under Contract No. DE-AC36-98GO 10337; at ORNL the work was sponsored by the Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation.

- ¹A. Hiraki, *Appl. Surf. Sci.* **56/58**, 370 (1992).
- ²H. Lange, *Mater. Res. Soc. Symp. Proc.* **402**, 307 (1995).
- ³F. M. D'Heurle and C. S. Petersson, *Thin Solid Films* **128**, 283 (1985).
- ⁴K. N. Tu, *Advances in Electronic Materials*, edited by B. W. Wessels and G. Y. Chin (American Society for Metals, Meta Park, OH, 1986), Chap. 7.
- ⁵C. I. Gregory, D. B. Lambrick, and N. R. Bernhoeft, *J. Magn. Magn. Mater.* **104/107**, 689 (1992).
- ⁶P. Lerch and T. Jarlborg, *J. Magn. Magn. Mater.* **131**, 321 (1994).
- ⁷P. Harris, B. Lebech, H. S. Shin, K. Mortensen, and J. S. Pedersen, *Physica B* **213/214**, 357 (1995).
- ⁸C. Thessieu, J. Flouquet, and G. Lapertot, *Solid State Commun.* **95**, 707 (1995).
- ⁹K. E. Sundstrom, S. Petersson, and P. A. Tove, *Phys. Status Solidi A* **20**, 563 (1973).
- ¹⁰M. Eizenberg and K. N. Tu, *J. Appl. Phys.* **53**, 6885 (1982).
- ¹¹L. Zhang and D. G. Ivey, *J. Mater. Res.* **6**, 1518 (1991).
- ¹²J. Wang, M. Hirai, M. Kusaka, and M. Iwami, *Appl. Surf. Sci.* **113/114**, 53 (1997).
- ¹³H. Tatsuoka, K. Isaji, K. Sugiura, H. Kuwabara, P. B. Brown, Y. Xin, and C. J. Humphreys, *J. Appl. Phys.* **83**, 5504 (1998).
- ¹⁴K. Matsuda, H. Katsuoka, K. Matsunaga, K. Isaji, H. Kuwabara, P. B. Brown, Y. Xin, R. Dunin-Borkowski, and C. J. Humphreys, *Jpn. J. Appl. Phys., Part 1* **37**, 6556 (1998).
- ¹⁵S. J. Pennycook and D. E. Jesson, *Phys. Rev. Lett.* **64**, 938 (1990).
- ¹⁶S. J. Pennycook and D. E. Jesson, *Ultramicroscopy* **37**, 14 (1991).
- ¹⁷K. Matsuda, Y. Takano, K. Kuwahara, H. Tatsuoka, Y. Yan, S. J. Pennycook, and H. Kuwabara (unpublished).
- ¹⁸R. A. Metzger and F. G. Allen, *Surf. Sci.* **137**, 397 (1984).
- ¹⁹O. Kubaschewski and C. B. Alcock, in *International Series on Materials Science and Technology: Metallurgical Thermo-chemistry*, 5th ed. (Pergamon, Oxford, 1979), Vol. 24, p. 294.
- ²⁰K. Fujita, S. Fukatsu, H. Yaguchi, T. Igarashi, Y. Shiraki, and R. Ito, *Jpn. J. Appl. Phys., Part 2* **29**, L39 (1990).
- ²¹Z. Jiang, A. Xu, D. Hu, H. Zhu, X. Liu, X. Wang, M. Mao, X. Zhang, J. Hu, D. Hung, and X. Wang, *Thin Solid Films* **321**, 116 (1998).