JOURNAL OF APPLIED PHYSICS VOLUME 91, NUMBER 8 15 APRIL 2002

Formation of MnSb during the growth of MnSi layers in the presence of an Sb flux

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(Received 27 August 2001; accepted for publication 23 January 2002)

Structural and compositional analyses of a MnSi layer have been performed to elucidate the growth mechanism. The MnSi layer was grown by reactive deposition epitaxy in the presence of an Sb flux. The existence of Sb was found at the MnSi/Si interface and on the surface of MnSi layer by secondary ion mass spectrometry. In addition, x-ray photoelectron spectroscopy measurement shows that MnSb is formed on the surface of the grown MnSi layer. On the atomic scale, scanning transmission electron microscopy observations reveal the existence of an Sb–Mn–Sb structure at the interface between the MnSi layer and the Si substrate. The formation of the MnSb plays an important role for the improvement of crystalline quality of the silicide layer, acting both as a surfactant and as a compliant substrate for stress relief.
[DOI: 10.1063/1.1461063]

I. INTRODUCTION

Epitaxial growth of silicide layers on Si substrates has attracted much attention due to their technological importance for microelectronic applications.[1] In addition, semiconducting silicides have generated interest as new semiconductor materials.[2] On the other hand, much less attention has been given to the silicides of the group VII elements in the periodic table. MnSi is an intermetallic compound which shows a magnetic transition at $T_C = 29.1$ K from a paramagnetic state to a helicoidal order.[3] An itinerant metamagnetic transition in MnSi has been observed,[4,5] and magnetic properties of MnSi under high pressure have been investigated.[6,7] There have been few reports, however, on the growth of MnSi. Growth of the silicides by reactive deposition epitaxy (RDE) or solid phase epitaxy have been performed previously.[8–11] Such procedures generally lead to the formation of many different polycrystalline silicide phases with an undulating interface between the silicide layer and the Si substrate, which emphasizes the difficulty of growing high quality silicide layers on Si substrates. Recently, Matsuda *et al.* developed a new growth technique, modified RDE, in the presence of an Sb flux for the growth of MnSi layers.[12] Then, this growth procedure was applied to the growth of epitaxial β-$FeSi_2$ layers and the improvement in structural quality of the layers was observed by Koga *et al.*[13]

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The details of growth mechanism of the layers, however, have not been clarified. In this article, experimental results of structural and compositional analyses of the MnSi layers grown by RDE using an Sb flux are reported to elucidate the growth mechanism.

II. EXPERIMENT

The MnSi layers were grown by simultaneous exposure of Si(111) substrates to Mn and Sb fluxes in a vacuum. The details of the growth procedure are described elsewhere.[12] The resultant layers were characterized using conventional transmission electron microscopy (TEM), and also *Z*-contrast scanning transmission electron microscope (STEM). 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). Under these conditions, the image intensity can be described accurately as a convolution between the electron probe and an object function sharply peaked at the positions of each atomic column, with a strength approximately the mean square atomic number (*Z*) of the column. Chemical concentration profiles at the interface between the layer and Si substrate were measured by secondary ion mass spectrometry (SIMS) using Cs^+ primary ions. Chemical composition and electronic states of the grown layer surface were examined by x-ray photoelectron spectroscopy (XPS) using Model:SSX-100 with a monochromatized Al $K\alpha$ source

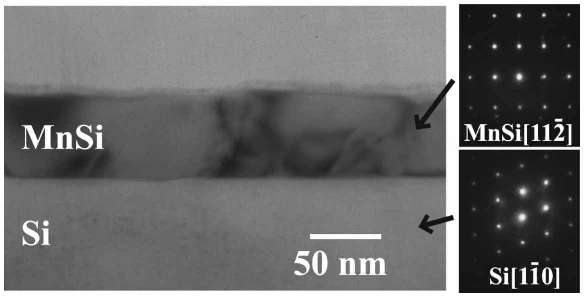

FIG. 1. Cross-sectional TEM image of the MnSi layer.

($h\nu$ = 1486.6 eV). The chemical composition was obtained from the corresponding core-level intensity taking into account the sensitivity factor.

III. EXPERIMENTAL RESULTS

Figure 1 shows a conventional cross-sectional TEM image of the resultant layer following Mn deposition and reaction with Si(111) at a temperature of 350 °C in the presence of the Sb flux. The diffraction pattern confirms the layer is single-crystal MnSi(111) and the interface is seen to be smooth. The epitaxial relationship between the MnSi layer and the Si substrate is given by $(111),[11\bar{2}]$MnSi//$(111),[1\bar{1}0]$Si. These results are consistent with TEM images shown in Ref. 12.

Figure 2 shows SIMS profiles of Mn and Sb for the layer grown in the presence of the Sb flux. The result reveals that the MnSi/Si/interface contains a large amount of Sb. It has been reported that Sb acts as a surfactant element which effectively suppresses island growth, and that Sb incorporation prevents roughening of the interface.[14,15] In addition, the existence of Sb on the silicide surface is also found by the SIMS profile, which will be discussed in connection with XPS results later.

Z-contrast STEM imaging of the interface revealed that Sb present at the interface formed a thin layer other than MnSi.[16] Figure 3(a) shows a *Z*-contrast image of the MnSi/Si interface viewed along the $[1\bar{1}0]$ zone axis of Si. In *Z*-contrast images, the intensity is proportional to the atomic number. The two bright lines at the MnSi/Si interface indicate that there is a thin layer containing an element that must be higher atomic number than Mn. The SIMS data suggest that this is Sb. Figure 3(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 and Si, indicating two monolayers of Sb. Figure 3(c) is an enlarged image showing details of the structure of the interface. It is seen that the thin layer at the interface has three planes parallel to the interface. Their intensities suggest that the two planes indicated by larger circles are two monolayers of Sb. In between, another monolayer is observed 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 monolayer of Mn is sandwiched by two Sb monolayers. It is noted that the structure of this Sb–Mn–Sb layer obtained from the *Z*-contrast image is consistent with a half unit cell of the MnSb crystalline lattice. The MnSi film then grow epitaxially on top of the second Sb monolayer. The two dark lines in Fig. 3(c) show how two planes of MnSi match the Sb–Mn–Sb structure. The first monolayer of Sb modifies the surface of the substrate. The Si columns at the surface no longer have dumbbell shape as indicated by the white arrow. The small increase of intensities for some Si columns at the Si surface suggests a small occupation of Sb in those columns.

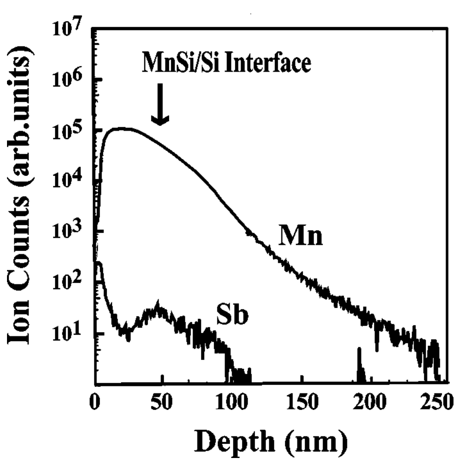

FIG. 2. SIMS profiles of Sb and Mn across the MnSi layer.

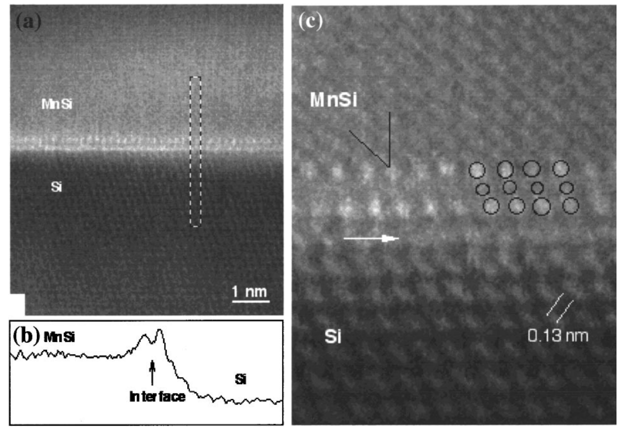

FIG. 3. (a) *Z*-contrast image of the MnSi/Si interface, (b) intensity profile measured from the dotted box region across the interface, and (c) atomic resolution *Z*-contrast image of the MnSi layer.

We now turn to an analysis of the surface of the film. Figure 4 shows chemical composition profiles of the MnSi layer measured by XPS. The depth was estimated by assuming the same sputter rate as for SiO_2. It is observed that Mn and Sb atoms coexist for about 1 nm. This result shows that a MnSb intermetallic compound is formed on the surface of the silicide layer, even though the optimum growth condition was chosen for the MnSi layer.[12] This has been reported previously for the case of high Mn deposition rate or low growth temperature.[17]

XPS valence band spectra of the surface of the MnSi film after sputtering for 0.1 and 15 nm are displayed in Figs. 5(a) and 5(b), respectively. The spectral features of Fig. 5(a) are a weak shoulder near the Fermi level (E_F) and peaks at

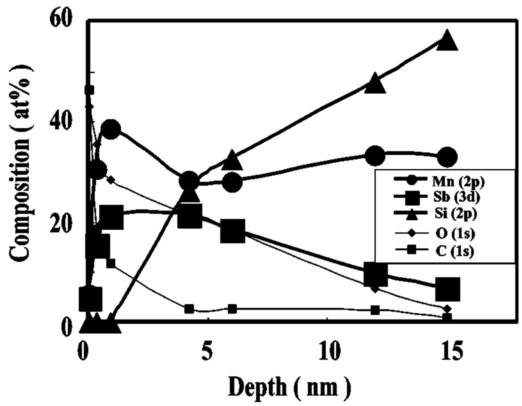

FIG. 4. Depth profile showing chemical composition of the MnSi layer deduced from XPS.

about 4 and 10 eV below E_F. On the other hand, the spectrum in Fig. 5(b) shows a strong density of states at E_F and a peak at about 9 eV. The valence band spectra of pure MnSb and MnSi compounds were measured by XPS to compare with the spectra shown, respectively, in Figs. 5(a) and 5(b) and are in good agreement with previous reports.[18,19] The features of Figs. 5(a) and 5(b) closely resemble those of MnSb and MnSi, respectively. A calculated band structure for MnSb (Ref. 19) is close to the spectra of Figs. 5(a) and 5(c). The shoulder near E_F corresponds to a cutoff in the Mn 3*d* density of states and the two peaks at about 4 eV and 10 eV correspond to a maximum in the density of Mn 3*d* upspins and Sb 5*s* states, respectively. For MnSi, theoretical calculation showed that the peak at about 9 eV can be ascribed to Si 3*s* states and the broad band at about 0–3 eV below E_F is due to Si 3*p* and Mn 3*d* states. This is in good agreement with the spectral features in Figs. 5(b) and 5(d). This result together with those from Fig. 4 suggests that MnSb is formed on the surface of the MnSi film.

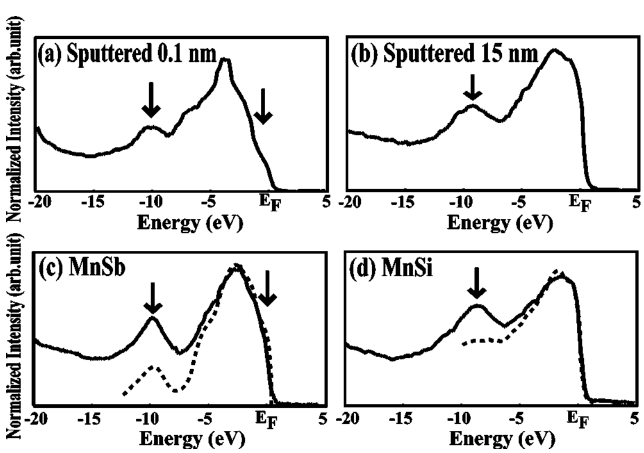

FIG. 5. XPS valence band spectra from the layer after sputtering (a) 0.1 nm and (b) 15 nm, and from bulk (c) MnSb and (d) MnSi, respectively. Dotted lines in (c) and (d) also show experimental XPS spectra (after Refs. 18 and 19), respectively.

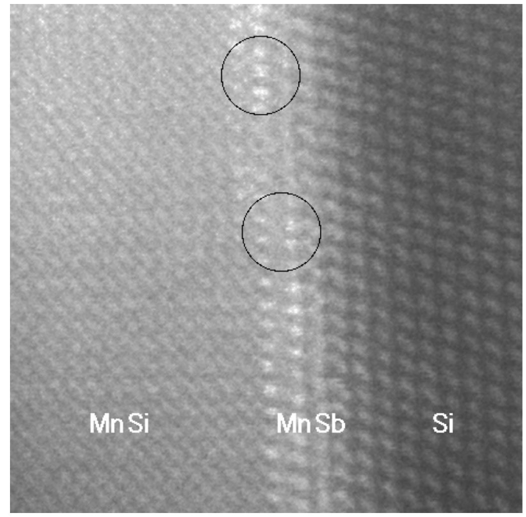

FIG. 6. *Z*-contrast image of the MnSb/Si interface showing the presence of interfacial dislocations.

IV. DISCUSSION

Recently, it has been reported that high quality MnSi layers with a smooth film/substrate interface can be grown in the presence of Sb flux.[12] We believe that the improvement in the crystalline quality and interface morphology is due to the action of the Sb as a surfactant during growth and in the formation of Sb-based intermetallic compounds. In this study, the surfactant element Sb was chosen for the following reasons. A surfactant should have a high vapor pressure and show a strong tendency to form intermetallic compounds. Then it will bind to metallic atoms and the formation of high-Mn silicides will be avoided. Furthermore, the intermetallic compound should have a low formation energy compared to the silicide, but should be stable at the silicide growth temperature. Group V-based intermetallic compounds meet these criteria.

In the Mn–Sb system, both MnSb and Mn_2Sb intermetallic compounds exist. However, it is known that MnSb(0001) epitaxial layers can be easily grown on Si(111) substrates in an Sb rich environment.[20] MnSb has a hexagonal NiAs-type crystal structure with lattice constants of $a = 0.4128$ nm and $c = 0.5789$ nm. On the other hand, MnSi has a cubic FeSi crystal structure ($a = 0.4556$ nm). The atomic spacing of the epitaxial MnSb along Si$[11\bar{2}]$, $d_{\mathrm{MnSb}} = \sqrt{3}/2\,a_{\mathrm{MnSb}} = 0.358$ nm, is larger than that of Si, $d_{\mathrm{Si}} = \sqrt{6}/4\,a_{\mathrm{Si}} = 0.333$ nm and also of the MnSi, $d_{\mathrm{MnSi}} = \sqrt{2}/2\,a_{\mathrm{MnSi}} = 0.322$ nm. The thin Sb–Mn–Sb layer observed in the *Z*-contrast image Fig. 3(b) is a half of a unit cell of the MnSb crystalline lattice. In addition, interface dislocations are visible between this layer and the substrate as shown in Fig. 6, which means that the MnSi layer is largely relaxed (except presumably for thermal mismatch stresses). The mechanism of the silicide growth is therefore considered to be as follows. The presence of the Sb flux means that the substrate surface is saturated with Sb before deposition of Mn. During the initial deposition of Mn, an epitaxial layer of the intermetallic MnSb is formed. This has a large lattice mismatch with the Si substrate, with a critical thickness less than one monolayer, so the layer relaxes immediately by the introduction of mismatch dislocations. Then, with subsequent deposition of Mn, a MnSi silicide layer is formed by interdiffusion of the MnSb layer and the Si substrate. The soft MnSb layer can easily adjust its lattice parameter to match that of MnSi without the need to introduce any new dislocations in MnSi. This explains why we observe interface dislocations only at the MnSb/Si interface. Excess surfactant atoms are reevaporated from the layer surface during the silicide growth. Thus, the surface and the interface layer are maintained rich in Sb.

As mentioned herein, the high quality silicide layers with a smooth interface have been grown, and the improvement in structural quality of the layer can be attributed to the following phenomena:

(1) Reduction in the migration distance of deposited atoms leads to the formation of a smooth layer, as with conventional surfactant growth.[14,15] The surfactant atoms suppress the migration of deposited atoms and the formation of islands.
(2) The phase formation depends not only on the equilibrium formation energy but also on interfacial composition and lattice mismatch between the silicide phase and Si matrix.[21] The high crystallographic symmetry between the Si(111) and predeposited MnSb(0001) enhances the formation of the MnSi phase. Generally, the Mn_5Si_3 phase is expected to be the first phase for a Mn–Si couple when Mn is deposited without an Sb flux.[22] In this case, nucleation of Mn-rich silicides at the initial stage of the growth leads to a sequence of polycrystalline phases.[9] Here, the MnSb(0001) encourages the formation of MnSi on Si(111) instead of other silicide phases.
(3) The MnSb is the initial phase formed on Mn deposition because of the excess Sb flux. Because of the high lattice mismatch the critical thickness of MnSb is less than one monolayer; misfit dislocations can be introduced directly at the interface as the monolayer islands of MnSb expand, so the film relaxes as it forms. Then, it can act as a *compliant substrate* for the subsequent epitaxial growth of MnSi. As the MnSi layer is formed, it too rapidly exceeds the critical thickness and again grows relaxed over the MnSb. This mechanism therefore avoids the generation of threading dislocations in the MnSi leading to a layer of high crystal quality.
(4) The interfacial plane between two different crystals is generally the one with low interface energy. The Si(111) plane is the closed packed plane and the Si(111) interface often appears between the silicide and Si couple. This means that the Si(111) plane is energetically stable. Moreover, hexagonal MnSb has a stable basal plane, namely MnSb(0001). This accounts for the smooth morphology after the silicide growth.

The growth procedure shown in this study is clearly successful as far as structural properties are concerned. However, the incorporation of surfactant atoms into the host materials must also be considered. For the case of conventional surfactant epitaxy, heavy incorporation of surfactant materials into grown semiconductor layers makes it difficult to control their electronic properties. In addition, the existence of a thin intermetallic interfacial layer might effect the electronic property of the silicide. Further investigation will be required to clarify the possibility of device applications using this growth procedure.

V. CONCLUSION

Surfactant-mediated RDE for silicide growth has been proposed and developed, furthermore structural and compositional analyses have been performed. Growth of the MnSi layer is accompanied by the formation of a MnSb intermetallic compound on the surface of the silicide layer, and three monolayers of this MnSb phase is also found at the interface between the silicide layer and Si substrate. This thin interfacial layer at the interface acts as a compliant substrate leading to a relaxed MnSi film free from threading dislocations and a smooth film/substrate interface. Further characterization of grown layers, however, will be required for applications to devices. This growth method would be useful for the growth of single-phase high quality epitaxial layers of other multiple phase alloys and may allow other new materials to be grown as thin films.

[1] H. Lange, *Silicide Thin Films—Fabrication, Properties, and Applications*, edited by R. T. Tung, K. Maex, P. W. Pellegrini, and L. H. Allen, Mater. Res. Soc. Symp. Proc. **402**, 307 (1995).
[2] V. E. Borisenko, in *Semiconducting Silicides: Materials Science* (Springer, Berlin, 2000).
[3] P. Lerch and T. Jarlborg, J. Magn. Magn. Mater. **131**, 321 (1994).
[4] H. Yamada and K. Terao, Phys. Rev. B **59**, 9342 (1999).
[5] K. Koyama, T. Goto, T. Kanomata, and R. Note, Phys. Rev. B **62**, 986 (2000).
[6] C. Pfleiderer, G. J. McMullan, S. R. Julian, and G. G. Lonzarich, Phys. Rev. B **55**, 8330 (1997).
[7] C. Thessieu, K. Kamishima, T. Goto, and G. Lapertot, J. Phys. Soc. Jpn. **67**, 3605 (1998).
[8] K. E. Sundström, S. Petersson, and P. A. Tove, Phys. Status Solidi A **20**, 563 (1973).
[9] M. Eizenberg and K. N. Tu, J. Appl. Phys. **53**, 6885 (1982).
[10] L. Zhang and D. G. Ivey, J. Mater. Res. **6**, 1518 (1991).
[11] J. Wang, M. Hirai, M. Kusaka, and M. Iwami; Appl. Surf. Sci. **113**, 53 (1997).
[12] K. Matsuda, H. Tatsuoka, K. Matsunaga, K. Isaji, H. Kuwabara P. D. Brown, and C. J. Humphreys, Jpn. J. Appl. Phys., Part 1 **37**, 6556 (1998).
[13] T. Koga, A. Bright, T. Suzuki, K. Shimada, H. Tatsuoka, and H. Kuwabara, Thin Solid Films **369**, 248 (2000).
[14] H. J. Osten, J. Klatt, G. Lippert, B. Dietrich, and E. Bugiel, Phys. Rev. Lett. **69**, 450 (1992).
[15] K. Fujita, S. Fukatsu, H. Yaguchi, T. Igarashi, Y. Shiraki, and R. Ito, Jpn. J. Appl. Phys., Part 2 **29**, L1981 (1990).
[16] Y. Yan, M. M. Al-Jassim, K. Matsuda, H. Tatsuoka, H. Kuwabara, and S. J. Pennycook, Appl. Phys. Lett. **75**, 2894 (1999).
[17] H. Tatsuoka, K. Isaji, K. Sugiura, H. Kuwabara, P. D. Brown, Y. Xin, and C. J. Humphreys, J. Appl. Phys. **83**, 5504 (1998).
[18] K. S. Liang and T. Chen, Solid State Commun. **12**, 957 (1977).
[19] W. Speier, E. v. Leuken, J. C. Fuggle, D. D. Sarma, L. Kumar, B. Dauth, and K. H. J. Buschow, Phys. Rev. B **39**, 6008 (1989).
[20] H. Tatsuoka, K. Isaji, H. Kuwabara, Y. Nakanishi, T. Nakamura, and H. Fujiyasu, Appl. Surf. Sci. **113**, 48 (1997).
[21] K. N. Tu, G. Ottaviani, R. D. Thompson, and J. W. Mayer, J. Appl. Phys. **53**, 4406 (1981).
[22] R. M. Walser and R. W. Bené, Appl. Phys. Lett. **28**, 624 (1976).