Epitaxial orientation of $Mg_2Si(110)$ thin film on Si(111) substrate

Y. Wang
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China and School of Engineering, The University of Queensland, St. Lucia QLD 4072, Australia

X. N. Wang, Z. X. Mei, and X. L. Du[a),b)]
Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

J. Zou[a),c)]
School of Engineering, The University of Queensland, St. Lucia QLD 4072, Australia and Centre for Microscopy and Microanalysis, The University of Queensland, St. Lucia QLD 4072, Australia

J. F. Jia and Q. K. Xue
Department of Physics, Tsinghua University, Beijing 100084, China and Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

X. N. Zhang and Z. Zhang
Beijing University of Technology, Beijing 100022, China

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Epitaxial $Mg_2Si(110)$ thin film has been obtained on Si(111) substrate by thermally enhanced solid-phase reaction of epitaxial Mg film with underlying Si substrate. An epitaxial orientation relationship of $Si(111) \parallel Mg_2Si(110)$ and $Si\langle 1\bar{1}0\rangle \parallel Mg_2Si\langle 1\bar{1}0\rangle$ has been revealed by transmission electron microscopy. The formation of the unusual epitaxial orientation relationship is attributed to the strain relaxation of Mg_2Si film in a $MgO/Mg_2Si/Si$ double heterostructure. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2821916]

Mg_2Si has promising applications in the infrared optoelectronic devices.[1] Many attempts have been made to prepare Mg_2Si films on Si substrates due to their potential applications.[2–4] However, the fact that Mg has a low condensation coefficient with Si and a high vapor pressure even at 200 °C ($\sim 10^{-7}$ mbar) makes it a formidable task to grow Mg_2Si epitaxial films on Si substrates.[1,5] In addition, the lattice mismatch between fcc Mg_2Si ($a=0.635$ nm) and Si ($a=0.539$ nm) is as large as 18%. As a consequence, no single-crystalline Mg_2Si thin film with a thickness over 1 nm has been satisfactorily achieved so far, although many efforts have been devoted to improve the growth methods.[1,6–8] Brause *et al.*[6] acquired a Mg_2Si layer on (111) Si without an epitaxial relationship between them. Hosono *et al.*[7] obtained polycrystalline Mg_2Si with predominant (211) texture by heating a bulk (111) Si under Mg vapor. By using molecular beam epitaxy (MBE), Mahan *et al.*[1] achieved a polycrystalline Mg_2Si thin film with (111) texture on both (111) and (100) Si substrates by codeposition of Mg with Si at 200 °C, and they found no accumulation of Mg or formation of Mg silicide on Si after reactive deposition of Mg onto the Si substrate at 200 °C. It has been reported by several researchers that $Mg_2Si(111)$ layer would form on Si(111) surface during the Mg deposition on Si(111).[8–10] In their reports, it was found that, to minimize the *in-plane* lattice mismatch between $Mg_2Si(111)$ and Si(111) planes, there was a 30° rotation between $Mg_2Si(111)$ and Si(111) planes along the [111] direction. However, the grown Mg_2Si layer can only be very thin ($\leqslant 0.6$ nm), otherwise, the Mg_2Si layer would be covered by metal Mg as Mg vapor continues. Until now, no uniform Mg_2Si thin film has been achieved on Si. In this study, we demonstrate the realization of an epitaxial $Mg_2Si(110)$ film on Si(111) in a MBE system. An unusual epitaxial relationship has been revealed. By using several techniques of transmission electron microscopy (TEM), the film formation mechanism has been investigated by focusing on the capping layer induced compressive strain in the Mg_2Si film.

The Mg_2Si thin films studied here were prepared by using the thermally enhanced solid-phase reaction of epitaxial Mg film with underlying Si(111) substrate in a radio frequency plasma-assisted MBE system (OmniVac).[11] Before being loaded into the growth chamber, the Si wafers were degreased in acetone and trichloroethylene, then etched with 5% HF solution for 5 min and rinsed in de-ionized water. A Mg film with a nominal thickness of ~ 6 nm was deposited on Si(111) with a rate of 0.2 Å/s under ultrahigh vacuum condition at −20 °C. Considering the high vapor pressure of Mg, a capping layer involving 4 nm thick MgO and 100 nm thick ZnO films was prepared on Mg layer to prevent Mg from reevaporation during the temperature ramping and annealing. After that, the sample was heated to 100 °C to enhance the solid-phase reaction between Mg and Si. Finally, an epitaxial Mg_2Si film was obtained after 3 h annealing at this temperature. The samples were investigated by cross-sectional TEM in a Philips CM200 field emission gun TEM

[a)]Authors to whom correspondence should be addressed.
[b)]Electronic mail: xldu@aphy.iphy.ac.cn.
[c)]Electronic mail: j.zou@uq.edu.au.

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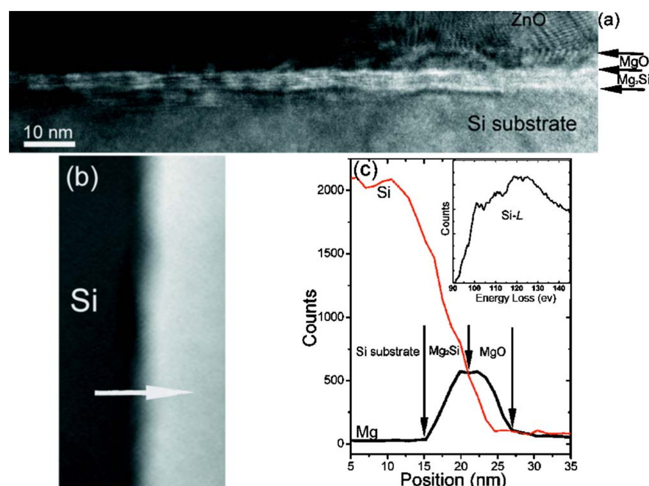

FIG. 1. (Color online) (a) A bright-field TEM image showing a uniform layer above the Si substrate. (b) A dark-field STEM image and (c) elemental profiles extracted from (b) showing distribution of elements (Si and Mg) within the film. The inset in (c) is the Si *L* edge of the EELS profile.

equipped with a Gatan image filtering system and a Tecnai F20 field emission gun TEM [equipped with a scanning functionality (STEM) and an energy dispersive spectroscopy (EDS)]. TEM specimens were prepared by the conventional mechanical grinding and polishing, followed by the ion beam thinning in a Gatan precision ion polisher system.

Figure 1(a) is a low magnification bright-field TEM image and shows the typical overview of the thin film with respect to the Si substrate. As indicated in the figure, a white thin layer with uniform thickness sandwiched between the Si substrate and the MgO topmost layer is clearly illustrated, and the MgO layer shows an island character. To understand the chemical component of these layers, STEM/EDS analyses were carried out and the results are shown in Figs. 1(b) and 1(c), respectively. Figure 1(b) is a dark-field STEM image in the area containing all epitaxial layers and the Si substrate. Figure 1(c) shows the EDS line-scan profiles of Si and Mg, respectively, along the growth direction [as indicated in Fig. 1(b)]. These profiles qualitatively demonstrate the variations of both elements across different layers, from which one can conclude that the layer adjacent to the Si substrate contains both Mg and Si. There is only one stoichiometric magnesium silicide phase, i.e., Mg_2Si, available in the Si-Mg phase diagram.[6] Besides, our EDS point analysis for this layer suggests a Mg/Si ratio of 2. This result was also confirmed by the electron energy loss spectroscopy (EELS) results [the inset of Fig. 1(c)], in which the Si *L* edge is similar to the Si *L* edge found in bulk Mg_2Si.[12] Therefore, we anticipate that this layer is Mg_2Si.

To understand the interface structure between Mg_2Si and Si at atomic level, high resolution TEM (HRTEM) was carried out. Figures 2(a) and 2(b) are typical HRTEM images taken along Si $[1\bar{1}0]$ and $[11\bar{2}]$ directions (both perpendicular to each other), respectively. A very sharp Mg_2Si/Si interface is observed, indicating a well-defined epitaxial layer of Mg_2Si with a thickness of ~3.5 nm, which is consistent with the observation on Fig. 1(a), where the thickness of the Mg_2Si layer is very uniform.

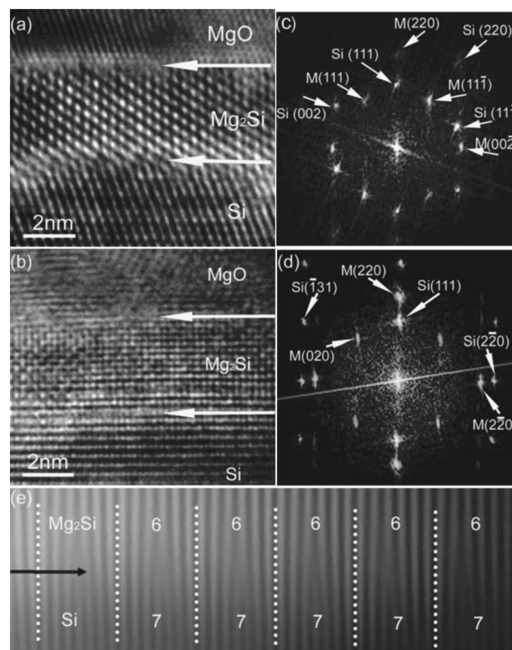

FIG. 2. Typical HRTEM images along (a) $Si[1\bar{1}0]$ and (b) $Si[11\bar{2}]$, respectively, showing atomic structures of the Mg_2Si thin film and its associated interfaces. [(c) and (d)] Fast Fourier transformations taken respectively from (a) and (b) in which the regions contain the Mg_2Si/Si interfaces. The diffraction spots indexed with M denote Mg_2Si. (e) A Fourier-filtered HREM image from (b) using diffraction spots $Si(2\bar{2}0)$ and $Mg_2Si(2\bar{2}0)$, showing every six $Mg_2Si(2\bar{2}0)$ planes match well with seven $Si(2\bar{2}0)$ planes (counted from the dotted lines).

To determine the epitaxial relationship between the Mg_2Si thin film and its underlying Si substrate, fast Fourier transformations (FFTs) (equivalent to the electron diffraction) were taken from the Mg_2Si/Si interfacial region of the HRTEM images as shown in Figs. 2(a) and 2(b),[13] and results are shown in Figs. 2(c) and 2(d), respectively. By careful indexing the two FFT patterns (as indicated in the FFT patterns, where *M* denotes Mg_2Si), the crystallographic orientation relationship between Mg_2Si and Si can be determined as $Si[111] \parallel Mg_2Si[110]$, $Si[1\bar{1}0] \parallel Mg_2Si[1\bar{1}0]$, and $Si[11\bar{2}] \parallel Mg_2Si[00\bar{1}]$.

To understand the nature of such an in-plane epitaxial relationship, we examined the equilibrium lattice mismatches $F_{Si\{hkl\}\parallel Mg_2Si\{h'k'l'\}} = (D_{Mg_2Si\{h'k'l'\}} - D_{Si\{hkl\}})/D_{Si\{hkl\}}$, where $D_{A\{hkl\}}$ is the lattice spacing of the $\{hkl\}$ atomic planes for material *A* in the two perpendicular in-plane directions. A schematic diagram of in-plane atomic structure [the $Mg_2Si(110)$ atomic plane superimposed with the $Si(111)$ atomic plane] is shown in Fig. 3. Based on their lattice parameters, $F_{3\times Si\{22\bar{4}\}\parallel Mg_2Si\{00\bar{2}\}} = -3.8\%$ and $F_{Si\{2\bar{2}0\}\parallel Mg_2Si\{2\bar{2}0\}} = 17.8\%$, in which the positive sign means that the epitaxial layer experienced a compressive stress and the negative sign indicates a tensile stress applied on the epitaxial layer. As can be expected, such lattice mismatches can generate significant misfit strains in different directions, particularly for the $[1\bar{1}0]$ direction, in which the lattice mismatch reaches 17.8%. To understand how this huge lattice mismatch was accommodated between Mg_2Si and Si, its interfacial structure was investigated. To do this, Fourier-filtered TEM image of the

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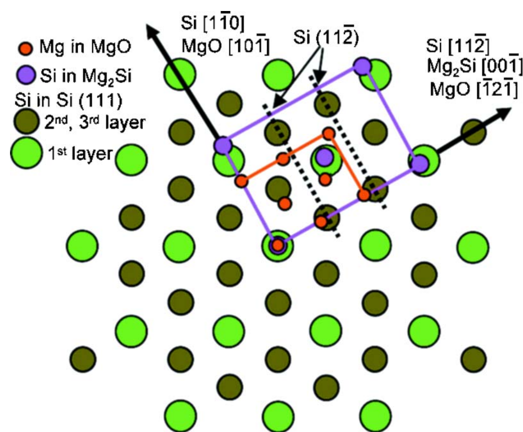

FIG. 3. (Color online) A schematic diagram showing the atomic arrangement of $MgO(111)/Mg_2Si(110)$ planes on Si(111) plane, where $Si[1\bar{1}0] \| Mg_2Si[1\bar{1}0] \| MgO[10\bar{1}]$ and $Si[11\bar{2}] \| Mg_2Si[00\bar{1}] \| MgO[\bar{1}2\bar{1}]$.

interfacial region[14] was acquired from Fig. 2(b) and the result is shown in Fig. 2(e). As can be clearly seen, for every seven $Si\{2\bar{2}0\}$ atomic planes, there were six Mg_2Si atomic planes to associate them (indicated by dotted lines), and such domain match periodically appeared. Based on the theoretical lattice parameters of Si and Mg_2Si, the $7\times\{2\bar{2}0\}_{Si}:6\times\{2\bar{2}0\}_{Mg_2Si}$ match can relieve a misfit strain of 16.8%, leaving a residual misfit strain (compressive) of 1% (17.8%–16.8%) in that direction. By such a $7\times\{2\bar{2}0\}_{Si}:6\times\{2\bar{2}0\}_{Mg_2Si}$ match, we have misfit strains (f) of $f=1\%$ in the $[1\bar{1}0]_{Si}$ direction and $f=-3.8\%$ in the $[11\bar{2}]_{Si}$ direction.

The question now is why and how the cubic Mg_2Si layer form in such an epitaxial relationship, but not as reported previously,[9,10] with Si during the annealing. To answer this question, we note that a $MgO(111)/Mg(0001)/Si(111)$ double heterostructure was formed at low temperature.[11] The annealing of this structure at 100 °C greatly enhanced the solid-phase reaction of the Mg film with the Si substrate due to the reactive nature of the Mg/Si interface even at room temperature, resulting in the formation of cubic Mg_2Si,[8,9] i.e., $MgO(111)/Mg_2Si/Si(111)$ structure was formed under this thermoequilibrium condition. It is anticipated that such a reaction drives the entire system toward to the stable situation (lower the system energy). To confirm this, we compare the misfit strains of the system before and after the annealing process. It has been reported[11] that the as-grown structure contains the Si substrate with the Mg layer and MgO layer on top of Si and they have an in-plane epitaxial relationship of $\langle 11\bar{2}\rangle_{Si} \| \langle 10\bar{1}0\rangle_{Mg} \| \langle 11\bar{2}\rangle_{MgO}$. Based on their lattice parameters, the lattice mismatches between Si and Mg can be estimated respectively as 26% in the $[11\bar{2}]_{Si}$ direction and −16% in the $[1\bar{1}0]_{Si}$ direction. As discussed above, the misfit strains between Mg_2Si and Si are −3.8% in the $[11\bar{2}]_{Si}$ direction and 1% in the $[1\bar{1}0]_{Si}$ direction (as most of the misfit strain in this direction has been relieved through the formation of regular misfit dislocations during the Mg_2Si formation), which is significantly lower than the Mg/Si case. In addition, the signs of in-plane misfit strains are opposite, i.e., compressive in one direction and tensile in the orthogonal direction, so that most of the in-plane misfit strains can be compensated within the interface by the in-plane distortion. In contrast, for the reported epitaxial relationship $[\{111\}_{Si} \| \{111\}_{Mg_2Si}$ and $\langle 110\rangle_{Si} \| \langle 112\rangle_{Mg_2Si}]$,[8,9] although the theoretical lattice mismatch is only ~2%, the Mg_2Si layer, in fact, experiences a compressive stress from all directions within the interface, which must be more significant than our case. This analysis suggests that our epitaxial relationship must be energetically favorable.

It is of interest to explore the role of MgO upon the formation of such an epitaxial relationship. Since the Mg_2Si layer is formed by the solid-phase reaction between Mg and Si, where MgO is a capping layer that prevents the desorption of Mg atoms during the annealing treatment and ensures the formation of such a uniform Mg_2Si layer. Interestingly, the MgO layer tends to have an epitaxial relationship with the underlying Mg_2Si, with MgO $(111)_{MgO} \| (110)_{Mg_2Si}$ and MgO $[10\bar{1}]_{MgO} \| [1\bar{1}0]_{Mg_2Si}$. Although the theoretical lattice mismatches in such an epitaxial relationship can be estimated respectively as ~7% in the $\langle \bar{1}2\bar{1}\rangle_{MgO}$ direction and −34% in the $\langle 1\bar{1}0\rangle_{MgO}$ direction, the fact that the MgO layer has a structural characteristic of islands suggests that the MgO layer can tolerate (e.g., relax) more distortion or a large amount of lattice mismatches induced during the reaction than the underlying Si substrate does. In addition, the ZnO overlayer should also play a similar role as the MgO on the formation of the Mg_2Si layer during the annealing.

In conclusion, single-crystalline Mg_2Si thin films have been achieved on (111) Si by the thermally enhanced solid-phase reaction of epitaxial Mg overlayer with Si substrate in a MBE system. An unusual epitaxial relationship between Si and Mg_2Si has been identified with $Si(111) \| Mg_2Si(110)$ and $Si[1\bar{1}0] \| Mg_2Si[1\bar{1}0]$.

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