Luminescent $FeSi_2$ Crystal Structures Induced by Heteroepitaxial Stress on Si(111)

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The crystal structures and the luminescent properties of $FeSi_2$ in the $FeSi_2/Si$ heteroepitaxial system have been investigated by first principles calculations. The results indicate that the heteroepitaxial β-$FeSi_2$ facing Si(111) by the (110) plane will be deformed from an orthorhombic to a monoclinic $P2_1/c$ structure with a γ angle of 95°. The strained crystal has a direct gap band structure and a finite oscillator strength of 0.7 between the band edges at the Y point. Since an indirect type band structure is obtained for other heteroepitaxial relationships, as well as for the bulk β-$FeSi_2$, we propose the strained $FeSi_2(110)/Si(111)$ structure to be the origin of the luminescence observed in the $FeSi_2/Si$ systems.

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The recent successful fabrication of the β-$FeSi_2$ light-emitting diode operating at a wavelength of 1.5 μm demonstrated potential capability of the silicide as a Si-based light-emitting material [1]. However, the origin of the light emission in β-$FeSi_2$ is not clearly understood.

In general, an efficient light-emitting material has a direct type band gap structure, so the type of the band gap structure for β-$FeSi_2$ is the first addressed question. Many experimental studies on the optical absorption of β-$FeSi_2$ have been reported, and most of them have argued β-$FeSi_2$ has a direct type band gap structure based on the energy dependence of the measured absorption coefficient [2]. However, some of them indicated that β-$FeSi_2$ has an indirect type band gap structure [3]. On the other hand, several first principles calculations on the electronic structure of β-$FeSi_2$ have been performed [4–12]. As discussed in the recent work of Moroni *et al.* [11], a full potential or a precise pseudopotential method is necessary to study the band structure of β-$FeSi_2$. By adopting such methods, Moroni *et al.* reported that β-$FeSi_2$ has an indirect type band structure with the top of the valence band at the Y point and the bottom of the conduction band at the Λ line [11]. Thus the type of the band gap structure for β-$FeSi_2$ is controversial.

An efficient light-emitting material has a large value of oscillator strength, so the value of the oscillator strength for β-$FeSi_2$ is the second addressed question. Only Eppenga [5] and we [12] have calculated the oscillator strength in β-$FeSi_2$. Eppenga obtained a finite value of the oscillator strength between the band edges along the Λ line by using the augmented spherical wave (ASW) method [5]. This result contradicts our calculation. Because we obtained zero values for the oscillator strength between the band edges not only for the Y point but also for the $\mathbf{k}$ points along the Λ line [12] by using the full-potential linearized augmented plane wave (FLAPW) method [13]. Thus the value of the oscillator strength for β-$FeSi_2$ is also controversial. As discussed in Ref. [12], the main difference between Eppenga's and our approaches is the treatment of the potential function, i.e., the atomic-sphere approximation (ASA) in Eppenga's calculation and the full potential in our calculation. In general, the full potential method is more precise than the method within the ASA. So the transitions between the band edges in the bulk β-$FeSi_2$ should be forbidden.

To date, the luminescence in β-$FeSi_2$ has been reported only in the β-$FeSi_2/Si$ heterostructures and only at the low temperatures [14,15], while no luminescence has been reported in the bulk β-$FeSi_2$ crystals. Those facts infer that the luminescence is not from the bulk β-$FeSi_2$ crystal but from the distorted crystal due to the heteroepitaxial relationship with the Si crystal.

The bulk β-$FeSi_2$ structure has the orthorhombic unit cell with the space group symmetry of *Cmca* and lattice parameters of $a = 9.863$ Å, $b = 7.791$ Å, and $c = 7.833$ Å [16]. It is known that there are three kinds of heteroepitaxial relations between β-$FeSi_2$ and the Si crystal which give a small misfit strain, i.e., β-$FeSi_2(100)/Si(001)$, β-$FeSi_2(110)/Si(111)$ (we shall label as type C), and β-$FeSi_2(101)/Si(111)$ (we shall label as type D) [17]. Recently, by using a plane wave basis method, Clark *et al.* studied the electronic structure of a strained β-$FeSi_2$ in which the lattice parameters are constrained according to the epitaxial relationship of β-$FeSi_2(100)/Si(001)$ [9]. However, they obtained indirect type band structures for the β-$FeSi_2$ in the type-A and -B relationships (see Ref. [9]). By using the linear muffin-tin orbital method with the ASA, Miglio *et al.* [10] studied three other heteroepitaxial structures on Si(111). They showed that the gap nature is turned from an indirect to a direct when β-$FeSi_2$ is strained according to the type-C relationship. They also reported that the indirect gap nature does not change in the β-$FeSi_2(100)/Si(111)$ and the type-D relationships. Thus the type-C structure is a candidate for the origin of the light emission from the $FeSi_2/Si$ systems. However, the oscillator strength for the strained structure has not been examined yet.

In this Letter, we investigate strained structures and luminescent properties of $FeSi_2$ on Si crystal by using first principles calculations. At first we examine band gap structures and oscillator strength for the strained structures studied by Clark *et al.* and Miglio *et al.* We show that the $FeSi_2$ is not luminescent while the crystal keeps the

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orthorhombic *Cmca* symmetry even if the crystal is strained. Next we determine the strained $FeSi_2$ structures on Si(111) by considering shear deformations. We obtain a direct type band gap structure and a finite value of oscillator strength for the sheared crystal, so that we propose the monoclinic $FeSi_2$ crystal as the origin of the luminescence observed in the $FeSi_2$/Si systems.

In order to determine the strained structure of $FeSi_2$ on Si(111) we adopted a plane wave basis set for ultrasoft pseudopotential (USPP) [18] with the generalized gradient approximations (GGA) [19] for the exchange-correlation functional. We employed the CASTEP code [20] to perform the calculations. The nonlinear core corrections were included [21] for the USPP of Fe. The special **k** points were sampled in the Brillouin zone (BZ) with the scheme of Monkhorst and Pack [22]. The **k** points were sampled at a density of 0.05 $Å^{-3}$ in the BZ, i.e., eight special **k** points for β-$FeSi_2$. The total energy converged to 0.02 eV per atom with respect to the total energy calculated with 18 special **k** points. For the basis, plane waves were used up to the cutoff energy of 280 eV. An increase to 300 eV changed the total energy by only 0.05 eV per atom.

To calculate the oscillator strength we adopted the FLAPW method based on the density functional theory within the local density approximation (LDA) for the exchange-correlation functional. We employed the WIEN97 code [23] to perform the calculations. Details of the calculation procedures were given in Ref. [12]. Within the electric dipole approximation, the oscillator strength between the one-electron eigenstates, m and n with the energies E_m and E_n, respectively, is described as $f_{mn}^{\alpha} = 4|\langle m|p_{\alpha}|n\rangle|^2/(E_m - E_n)$, where the energies are in units of Rydberg and p_{α} is the α component ($\alpha = x, y, z$) of the momentum operator in atomic units. Although we did not examine the symmetry of the irreducible representation of the eigenstates, we considered the transition as a forbidden one when the transition probability $|\langle m|p_{\alpha}|n\rangle|^2$ was smaller than 10^{-15}. Such a small value comes only from numerical errors. The zero values in the tables represent such small values.

First, we examined, by using the FLAPW, the strained structures studied by Clark *et al.* [9] and Miglio *et al.* [10]. In both of the strained structures, distortions of the lattice parameters were considered, but the crystals were kept in the orthorhombic *Cmca* symmetry as well as the bulk β-$FeSi_2$. The results are compiled in Table I. The band gaps are smaller than the values obtained by Clark *et al.* and Miglio *et al.* We also found other discrepancies in the topology of electronic structures. However, the important point is that, for all those structures, we obtained zero values of the oscillator strength between the band edges at the Y point and along the Λ line. It means that the transitions are forbidden at the band edges, in those strained structures.

TABLE I. Calculated electronic band structures for the structures considered by Clark *et al.* and Miglio *et al.* The 64th and the 65th bands are the valence band maximum and the conduction band minimum, respectively.

Type	**k** point	E_{64} (eV)	E_{65} (eV)	Gap	$f_{64\text{-}65}$
A	Y	0	+0.56	Direct	0
	Λ	−0.08	+0.77	At Y	0
B	Y	0	+0.45	Indirect	0
	Λ	−0.27	+0.37		0
C	Y	0	+0.25	Direct	0
	Λ	−0.23	+0.33	At Y	0
D	Y	0	+0.59	Quasidirect	0
	Λ	+0.10	+0.22	On Λ	0

Clark *et al.* [9] adjusted the lattice parameters of β-$FeSi_2$ to the Si(001) surface, and considered relaxation of the lattice to the direction perpendicular to the Si(001) surface. But the strained crystal was kept in the orthorhombic *Cmca* symmetry. Miglio *et al.* [10] adjusted the lattice parameters of β-$FeSi_2$ to the Si(111) surface. But they considered only the uniform dilatations for the strained β-$FeSi_2$ structures of the type-C and -D relationships, so that the strained crystals were also kept in the orthorhombic *Cmca* symmetry. However, the crystal symmetry of the strained β-$FeSi_2$ on Si(111) should be changed according to the relaxation perpendicular to the Si(111) surface. For the type-C and -D, the space group symmetry of the $FeSi_2$ structures should be changed from the orthorhombic *Cmca* to the monoclinic $P2_1/c$ and $C2/c$, respectively, caused by the strain along the [112] direction of Si crystals. In general, a forbidden transition becomes an allowed one if the symmetry of the structure is lowered. Therefore, it is inferred that the recombination at the band edge(s) might be allowed

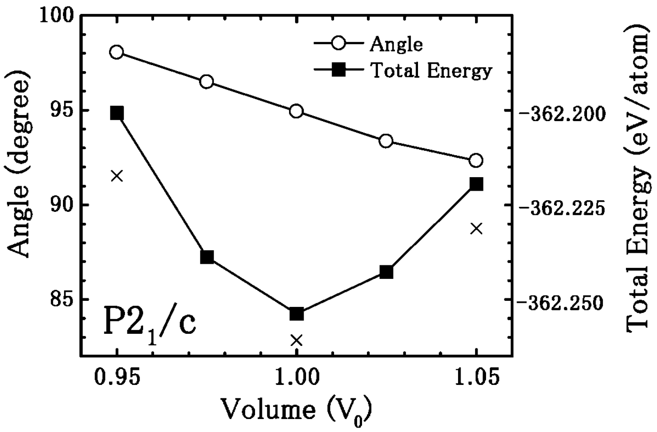

FIG. 1. Total energy of the $P2_1/c$ structure of $FeSi_2$ depending on the angle γ at several volumes. V_0 denotes volume of the bulk β-$FeSi_2$. The notation × denotes the results of relaxation of atomic configuration in the unit cell.

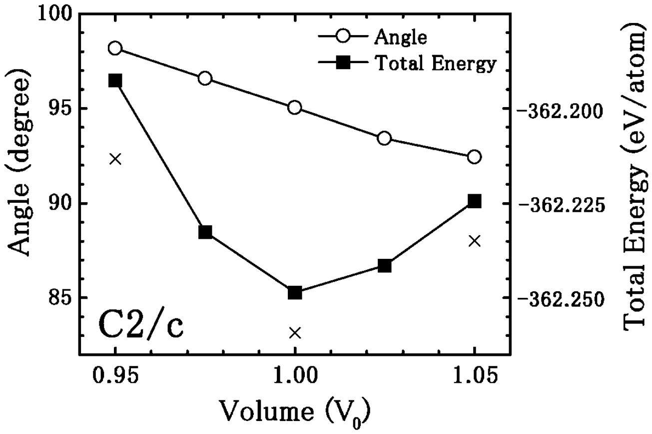

FIG. 2. Total energy of the $C2/c$ structure of $FeSi_2$ depending on the angle β.

for the monoclinic $FeSi_2$ structures. In addition, it is important to note that such a symmetry lowering is not expected for the other heteroepitaxial relationships, such as β-$FeSi_2(100)/Si(001)$ and β-$FeSi_2(100)/Si(111)$.

Based on the above considerations, we investigated the monoclinic $FeSi_2$ structures induced by the heteroepitaxial stress on Si(111). The calculations are performed by the plane wave basis method. In the calculations, at first we assumed the same atomic configuration as the bulk crystal in the unit cell. The c and b axes are fitted to twice the interatomic distance on Si(111) along the $[1\bar{1}0]$ direction (7.68 Å) of Si crystals for the $P2_1/c$ and $C2/c$ structures, respectively. The distances of $(a^2 + b^2 - 2ab\,\cos\gamma)^{1/2}$ and $(a^2 + c^2 - 2ac\,\cos\beta)^{1/2}$ are fitted to twice of the interatomic distance on Si(111) along the [112] direction (13.30 Å) of Si crystal for the $P2_1/c$ and $C2/c$ structures, respectively. In the constant volume condition, the total energy values are functions of the angle between the a and b axes (γ) and between the a and c axes (β) for the $P2_1/c$ and $C2/c$ structures, respectively. Figure 1 shows the calculated total energy of the $P2_1/c$ structure as a function of the angle γ at several constant volumes. We obtained the value of 95°, and almost the same volume as the bulk crystal, for the most stable structure. The obtained values of the c, a, and b axes are 7.68 Å (−2.0%), 10.16 Å (+3.0%), and 7.74 Å (−0.6%), respectively. Here, the numbers inside the parentheses indicate the changes with respect to the values of the bulk β-$FeSi_2$. Figure 2 shows the same relationships as Fig. 1 for the $C2/c$ depending on the angle β. Again the structure is most stable at the angle of 95°, and at almost the same volume as the bulk crystal. The obtained values of the b, a, and c axes are 7.68 Å (−1.6%), 10.16 Å (+3.0%), and 7.74 Å (−1.1%), respectively. In both cases, we see that the b and the c axes are shortened and the a axes are elongated. We can consider that the uniaxial stress along the direction parallel to the Si(111) surface is compensated by the shear. In Figs. 1 and 2, the symbols × indicate points after relaxations of the atomic configurations in the unit cells. The energy values are changed only a few ten meV per atom by the relaxations. Also the energy shifts during the relaxations are comparable at the different volumes. So the angles and volumes of the most stable structures are not changed by the relaxations. The $P2_1/c$ structure is more stable than the $C2/c$ structure by an energy difference of only 4 meV per atom, i.e., 0.1 eV per unit cell of Fe_8Si_{16}.

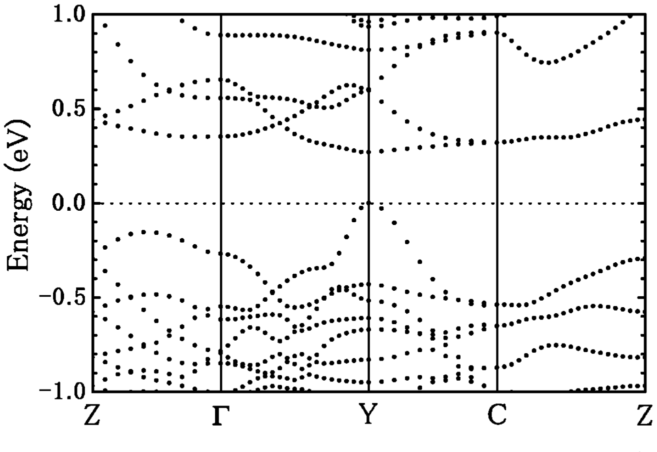

FIG. 3. Electronic band structure of the relaxed $P2_1/c$ structure.

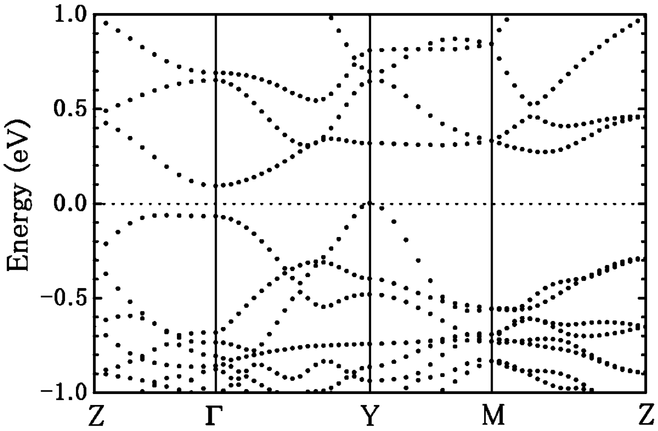

FIG. 4. Electronic band structure of the relaxed $C2/c$ structure.

TABLE II. Calculated electronic band structures for the monoclinic $FeSi_2$. The transitions are allowed only via z and y components of momentum for the $P2_1/c$ and the $C2/c$ structures, respectively. The oscillator strength on the Γ-Z line is evaluated at the middle point.

Type	**k** point	E_{64} (eV)	E_{65} (eV)	Gap	$f^{\alpha}_{64\text{-}65}$
$P2_1/c$	Y	0	+0.27	Direct	0.69
	Γ-Z	−0.15	+0.35	At Y	1.0×10^{-3}
$C2/c$	Y	0	+0.32	Indirect	0.49
	Γ	−0.07	+0.09		3.6×10^{-5}
	Γ-Z	−0.06	+0.09		4.5×10^{-3}

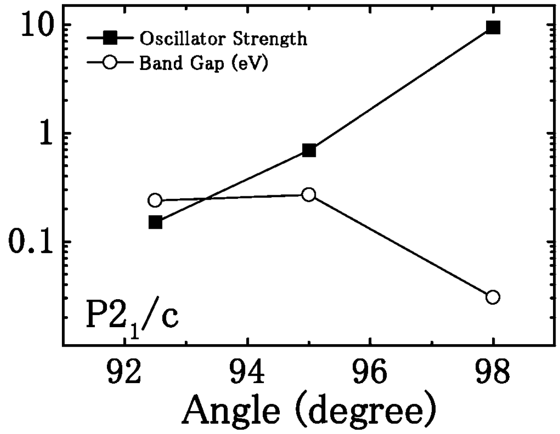

FIG. 5. The oscillator strength and the band gap energy, at Y point, versus the angle γ of the relaxed $P2_1/c$ structures at $V/V_0 = 1.05$, 1.0, and 0.95. For the relation between relative volume and angle, see Fig. 1.

In Figs. 3 and 4 we show the band structures calculated by the FLAPW for the most stable structures after the relaxations of the atomic configurations. We obtained direct and indirect type band structures for the $P2_1/c$ and $C2/c$ structures, respectively. In Table II, the results of the transition energy and the oscillator strength are compiled. For both structures, finite values of the oscillator strength between the band edges were calculated at the Y point and at the point between Γ-Z. We obtained the maximum value of the oscillator strength, namely 0.7, at the Y point, in the $P2_1/c$ structure. We propose this transition as the origin of the light emission from $\mathrm{FeSi_2}$ observed in experiments, because it is the only band edge transition, among the examined structures, in a direct band structure with a finite oscillator strength.

There is a discrepancy between the photon energy observed in the experiments, about 0.8 eV, and the calculated band gap energy, 0.27 eV, which might come from the characteristic underestimation of gaps in the LDA [24]. However, this should not change our conclusion. Furthermore, as shown in Fig. 5, the oscillator strength increases as the γ angle increases. Also the changes of the band structures are not drastic during the deformations from the bulk β-$\mathrm{FeSi_2}$ to the strained structures. Particularly, the sequence of the eigenvalues at the band edges does not change. So it looks that the oscillator strength became finite because the symmetry of the wave functions at the band edges changed due to the symmetry lowering of the structures.

In conclusion, we have shown that the heteroepitaxial β-$\mathrm{FeSi_2}$ facing to Si(111) by the (110) plane is deformed from the orthorhombic to the monoclinic $P2_1/c$ structure which has the direct type band structure and the finite oscillator strength value of 0.7.

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