Temperature dependence of direct transition energies in $\beta$-FeSi$_2$ epitaxial films on Si(111) substrate

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Abstract

Temperature dependence of direct transition energies ($E_g$) was investigated in $\beta$-FeSi$_2$ epitaxial films on Si(111) substrate. The lattice volume of the epitaxial films was reduced as the annealing temperature ($T_a$) increased. In photoreflectance measurements, the samples annealed at higher $T_a$ showed a larger temperature dependence of $E_g$. These results revealed that the temperature dependence of $E_g$ depended on the lattice deformation by the thermal annealing. The fact supports the band gap modifications by the lattice deformation.

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1. Introduction

$\beta$-FeSi$_2$ has attracted much interest as silicon-based optoelectronics material because it shows photoluminescence (PL) and photoresponse at 1.54 $\mu$m [1]. But the electronic structure of $\beta$-FeSi$_2$ epitaxial films on Si substrate has been not well understood. Since $\beta$-FeSi$_2$ can be viewed as a moderate distortion of the CaF$_2$ structure by way of the Jahn-Teller effect [2], the electronic structure should be affected by the stress at the heteroepitaxial interface of $\beta$-FeSi$_2$/Si [3]. Recently, in $\beta$-FeSi$_2$ epitaxial films on Si(111) substrate, we have reported a red shift of direct transition energies ($E_g$) and a lattice deformation when the annealing temperatures ($T_a$) increased [4]. The red shift of $E_g$ revealed a band gap modification by the lattice deformation. Assuming that the lattice deformation depending on $T_a$ originates from a reduction of the lattice mismatch at the $\beta$-FeSi$_2$/Si interface, the dependence of the lattice contraction on measurement-temperature should also depend on $T_a$. Therefore, it is expected that the temperature dependence of $E_g$ is different in the annealed samples.

In this study, we have investigated the temperature dependence of $E_g$ in the annealed $\beta$-FeSi$_2$/ Si(111) epitaxial films to confirm the band gap modification by the lattice deformation.

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2. Experiments

$\beta$-FeSi$_2$ epitaxial film was grown on n-type floating-zone Si(111) substrate ($\rho = 2.5$-3.0 kΩ cm) by molecular beam epitaxy (MBE) using template technique. The details of the epitaxial growth are described elsewhere [4]. After the epitaxial growth, the film was annealed at $T_a = 700$ and 900 °C for 16 h in a vacuum of $\sim 10^{-5}$ Pa. The crystal structure of the films was analyzed by high-resolution X-ray diffraction (HRXRD : X’pert Pro, PANalytical) at room temperature. The lattice constant of $a$-axis was obtained by the $\beta$-FeSi$_2$(800) peak position, and that of $b$- and $c$-axis were evaluated by the peak separation of the $\beta$-FeSi$_2$ (406)(460) peaks [5]. In PR measurements, a halogen lamp in conjunction with a single grating monochromator was used as a probe source. The pump source was 532 nm laser mechanically chopped at a frequency of 140 Hz. The modulated reflection signal ($\Delta R/R$) was detected by an InGaAs photodiode. In the low-electric-field, the $\Delta R/R$ for three dimensional transition is given by a generalized Lorentzian function called the Aspnes third derivative functional form [6],

$$\Delta R/R = \text{Re} \left[ \sum_j C_j e^{i\theta_j} (E - E_j + i\Gamma_j)^{-m} \right]$$

, where $E_j$ is direct transition energy, $\Gamma_j$ is broadening parameter. $C_j$ and $\theta_j$ are amplitude and phase factor, respectively. The exponent $m$ is fixed at 2.5 for a three-dimensional transition. By a least-square fitting to PR spectra using Eq. (1), direct transition energies were obtained at the range of 5.5–180 K.

3. Results and Discussion

In the XRD measurements, the as-grown films showed highly $\beta$-FeSi$_2$(110)/(101)-oriented film on Si(111). The full width at half maximum (FWHM) of rocking curve corresponding to $\beta$-FeSi$_2$ (220)/(202) diffraction peak was 0.24˚. In the as-grown sample, the lattice constant of $a$-axis is expanded by $\Delta a/abulk = +0.85\%$ compared to that of a single crystal ($abulk$), and $b$- and $c$-axis are compressed by $\Delta b/b_{bulk} = -0.23\%$ and $\Delta c/c_{bulk} = -0.71\%$, respectively. As $T_a$ increases, lattice constant of $a$-axis is more expanded, and those of $b,c$-axes are more compressed. These results show that all the lattice constants of the epitaxial film deviate from those of the single crystal by the thermal annealing. The changes of the lattice constants result in the volume reduction in -0.2% (Fig. 1(a)). This lattice deformation could be understood qualitatively by the lattice mismatch between $\beta$-FeSi$_2$ and Si(111) substrate. In the epitaxial growth of $\beta$-FeSi$_2$ on Si(111), two epitaxial relationships of type A: $\beta$-FeSi$_2$(101) || Si(111) with $\beta$-FeSi$_2$(010) || Si (011) and type B: $\beta$-FeSi$_2$(110) || Si(111) with $\beta$-FeSi$_2$(001) || Si (011) have been reported [7]. When we assume the type A epitaxial growth in the samples, the lattice mismatch between $\beta$-FeSi$_2$ single crystal and Si is defined as $\delta_1 = +1.4\%$ along the Si[110] direction and $\delta_2 = -5.3\%$ along the Si[112] direction, respectively.
Figure 1(b) shows the $\delta_1$ as a function of $T_a$ in the samples. The $\delta_1$ decreases from +1.32% (as-grown) to +1.17% ($T_a = 900^\circ$C), while $\delta_2$ is almost constant at -4.9% (not shown). From these results, it could be understood that the reduction of $\delta_1$ during the thermal annealing causes the lattice deformation.

Figure 2 shows PR spectra at 5.5 K in the sample annealed at $T_a = 900^\circ$C. As a result of the fitting (dashed lines), two transition energies of $E_g = 0.910$ eV and $E_i = 0.880$ eV were obtained. The $E_g$ is assigned as the direct interband transition energy in $\beta$-FeSi$_2$. The origin of $E_i$ is uncertain, but is suggested to be an impurity- or a defect-related transition [8]. As reported before [4], these transition energies shifted to lower photon energy as the $T_a$ increases. The red shift shows that the direct band gap is modified by the lattice deformation during the thermal annealing.

Figure 3 shows the temperature dependence of PR spectra in the as-grown sample. The PR spectra shift to lower energy as temperature increases. The $E_g$ and $E_i$ at each temperature were obtained by the fitting using Eq.(1).

Figure 4 and 5 show the temperature dependence of $E$ in the as-grown sample. The PR spectra shift to lower energy as temperature increases. The $E_g$ and $E_i$ respectively. In the figures, the energies in the samples annealed at 700 °C and 900 °C are also shown. In Fig. 4, for comparison, direct energy gaps measured in the $\beta$-FeSi$_2$ single crystal [9] are shown by the dashed line. The $E_g$ in the epitaxial films is smaller than the single crystal. The result suggests the difference in the band structure between the epitaxial film and the single crystal. In the epitaxial films, the $E_g$ in the annealed films shows larger energy variation than the as-grown sample with increase of measurement temperature. On the other hand, the $E_i$ doesn’t show a noticeable difference between the samples. The following empirical law (the Varshni’s formula) has been employed to analyze the temperature dependences of the band gap,

$$E(T) = E(0) - \alpha T^2 / (\beta + T) \quad (2)$$

, where $E(0)$ is the band gap at 0 K, $\alpha$ is an energy shift coefficient for temperature and $\beta$ is a constant [10]. The obtained Varshni’s parameters are listed in Table 1. The sample annealed at higher $T_a$ shows larger $\alpha$ in the $E_g$. The results convince us that the temperature dependence of $E_g$ depends on the $T_a$.

In the temperature dependence of the band gap in semiconductors, two effects contribute to the red shift of the band gap. The first effect is due to an electron-phonon interaction and the second is a thermal expansion. Considering these two effects, the total energy shift can be described as follows [11],

$$[\partial \Delta E/ \partial T]_p = [\partial \Delta E/ \partial T]_r + [\partial \Delta E/ \partial V]_T \cdot [\partial V/ \partial T]_p \quad (3).$$

The first and second terms in the right side represent the effect of the electron-phonon interaction and the thermal contraction of the lattice volume, respectively. In the epitaxial films, the lattice constants in $a$-axis were more expanded as the $T_a$ increased. In that case, the contraction along to $a$-axis is considered to be enhanced in the sample annealed at higher $T_a$ because the linear thermal expansion coefficient is the largest in $a$-axis of $\beta$-FeSi$_2$ [12]. Therefore, the thermal contraction of the lattice volume would be enhanced in the sample annealed at higher $T_a$ by
the shrinkage in $a$-axis. Considering Eq. (3), the larger $\Delta$ of $E_g$ in the annealed samples is understood by the thermal contraction of the lattice volume. The clear correlation between the lattice volume and the direct transition energy of $\beta$-FeSi$_2$ convince us that the electronic structure could be modified by the stress at the heteroepitaxial interface of $\beta$-FeSi$_2$/Si.

4. Conclusions

We conducted the PR measurements in $\beta$-FeSi$_2$ epitaxial films on Si(111) at temperatures from 5.5 to 180 K. The direct transition energy of $\beta$-FeSi$_2$ showed difference temperature dependence depending on the annealing temperature. The temperature dependence of the direct transition energy could be understood by the lattice deformation. These results support the possibility of band gap modifications by lattice deformation in $\beta$-FeSi$_2$ epitaxial films.

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