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OPTICAL PROPERTIES OF β-FESI$_2$ SEMICONDUCTING LAYERS[1]

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Optical transmittance and reflectance measurements have been carried out on semiconducting β-iron disilicide layers formed by annealing of Fe films evaporated onto silicon substrates and capped with amorphous silicon thin overlayers and by codeposition of Fe and Si onto a glass substrate. The dependence of the absorption coefficient on the energy of photons favours direct allowed transitions with the forbidden energy gap of (0.87±0.04) eV at the room temperature. The application of a simple three-parameter semiempirical formula to the temperature dependence of the direct energy gaps leads to the following best fitting parameters; the band gap at zero temperature $E_g(0) = (0.895 \pm 0.0037)$ eV, the dimensionless coupling parameter $S = 2.01 \pm 0.27$, and the average phonon energy $\langle \hbar\omega \rangle = (46.0 \pm 8.17)$ meV (averaging for four samples). Comparison of these parameters with those reported for β-$FeSi_2$ indicates that, although the band gaps at zero temperature are very similar, both the coupling parameters and the average phonon energy may vary if samples are fabricated by different techniques and thermal processes.

1 Introduction

There has been a growing interest in properties of semiconducting β-$FeSi_2$ in recent years due to its compatibility with silicon technology and due to its reported direct band gap for possible applications in silicon-based optoelectronic components [1,2]. Several phases can be grown by reaction with the Si substrate: Fe_3Si (poor metal), FeSi (narrow gap semiconductor), β-$FeSi_2$ (semiconductor) and α-$FeSi_2$ (metal). The β-iron disilicide can be fabricated either on (001) Si or (111) Si substrate using different

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techniques, such as solid phase epitaxy (SPE) [3], reactive deposition epitaxy (RDE) [4], ion beam synthesis (IBS) [5], molecular beam epitaxy (MBE) [6], chemical beam epitaxy (CBE) [7], or pulsed laser deposition (PLD) [8]. Structural and electrical studies over the last few years have indicated that the properties of β-$FeSi_2$ vary considerably if different growth techniques and different subsequent thermal treatment were applied. In this paper, we describe optical properties of β-$FeSi_2$ layers.

Calculations of the electronic structure of β-$FeSi_2$ show that this material is a semiconductor with an indirect gap of 0.8 eV [9] or 0.44 eV [10]. From low temperature measurements, Giannini et al. [11] and Rademacher et al. [12] have demostrated the existence of an indirect gap a few tens of meV lower than the direct one. The difference between the theoretically calculated indirect and direct gaps is about 35 meV [9] or 20 meV [10]. Furthermore, by calculating the shifts in the energies induced by small changes in the atomic positions, Christensen [9] illustrated a strong coupling to the lattice. The idea of a particularly strong interaction between the band-edge states and the phonons in β-$FeSi_2$ is further substantiated by the large dependence of the direct gap on temperature [11]. While the slope of band gap vs T at high temperatures as determined by Arushanov et al. [13] on single crystals is in good agreement with the value determined by Waldecker, Meinhold and Birkholz [14] at 700-1200 K temperatures on samples prepared by powder metallurgical techniques (bulk polycrystalline material), it is more than two times smaller than the value determined by Giannini et al. [11] on polycrystalline films. Recently, also Yang et al. [15] published that, although the band gaps at 0 K are very similar, both the lattice coupling constant and the average energy in ion beam synthesized polycrystalline semiconducting β-$FeSi_2$ on (001) Si are much smaller than those of Giannini et al. [11].

2 Experimental

The sample preparation and measuring techniques have been described earlier [16,17]. The silicides were formed by annealing an iron film evaporated onto silicon substrates and capped either with amorphous silicon or with SiO_x thin overlayers and by codeposition of Fe and Si onto glass substrate at 500 °C (sample D). In the experiments (100) Si 6-10 Ωcm and (111) Si 2-4 Ωcm p-type (B doped) and (111) Si 2-6 Ωcm n-type (P doped) wafers were used as substrates. The thickness of deposited iron films was 90-150 nm [17]. The annealing was carried out in IC grade purity nitrogen at atmospheric pressure for 2 h at 800 or 650 °C. The capping layers were removed after the annealing of samples. The optical transmission spectra in the region of the photon energy from 0.37 to 1.3 eV (3.333-0.954 μm) were obtained by the Carl Zeiss instrument Specord 61 NIR in the temperature interval from 80 to 380 K. The reflectance measurements were carried out for small samples in the region of 0.65 to 1.18 eV (1.9-1.05 μm) using an Al mirror as a reference surface only at room temperature.

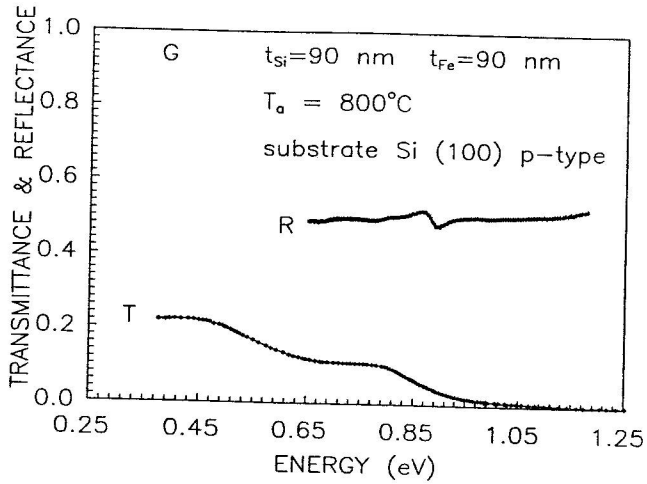

Fig. 1. Reflectance and transmittance spectra of β-$FeSi_2$ film formed by annealing deposited Fe film at T_a = 800°C measured at room temperature. t_{Fe} and t_{Si} are thicknesses of as-deposited Fe film and a-Si capping, respectively.

3 Results and discussion

Near-infrared reflectance and transmittance spectra for one of the samples is shown in Fig. 1. The transmission curves demostrate that the samples are transparent for the photon energy values less than 0.95 eV. Below this energy, the reflection spectra show interferences caused by the reflection at the surface and interface of the β-$FeSi_2$/Si structure. Since the thickness of the β-$FeSi_2$ films is small, the methods utilising interference fringes versus the photon wavelength to yield the index of refraction and the exact thickness and absorption coefficient are not applicable. In the energy range around the fundamental edge of the silicide the absorption of the silicon substrate is negligible. Consequently, as in [18] and [19], we calculate the absorption coefficient using the approximate formula

$$\alpha t = \ln \frac{1-R}{T}, \tag{1}$$

where α is the absorption coefficient of the silicide, $t \equiv t_{\beta-FeSi_2}$ is the thickness of the silicide layer, R and T are the measured reflectance and transmittance, respectively. This simplification is valid only for rather high values of the absorption in the silicide layer when the reflections of light at the silicide/Si substrate interface and at the free surface of the Si-substrate are still negligible. This case corresponds to the onset of the absorption edge.

In the case of the samples A, B, C and D, we have calculated the absorption coefficient using the approximate expression [17]

$$\alpha t = \ln \frac{(1-R_1)(1-R_{1/2})(1-R_2)}{T}, \tag{2}$$

where $R_1 \approx R$ and T are the measured reflectance and transmittance, respectively, $R_{1/2}$ is the reflectance at the β-$FeSi_2$/Si or β-$FeSi_2$/glass interface and R_2 is the reflectance at the free surface of the substrate.

The quantity $(\alpha Et)^2$ as a function of the photon energy E is shown in Fig. 2. The data are plotted in a manner giving a linear part of the curve for the direct allowed transitions with the fundamental absorption fulfilling the formula

$$(\alpha Et)^2 = (Kt)^2(E - E_g), \tag{3}$$

where K is a parameter depending on details of the band structure and E_g is the forbidden gap energy. The extrapolation toward the point where $\alpha = 0$ gives E_g. These extrapolations together with their parameters are shown in Fig. 2. The Fe-layer thicknesses were determined using the Rutherford backscattering spectroscopy (RBS) analysis of samples [17]. Owing to some uncertainty of the thickness we preferred to plot the quantity $(\alpha Et)^2$ instead of $(\alpha E)^2$. The direct optical gap has the average value $E_g = (0.87 \pm 0.04)$ eV (standard deviation is equal to 0.025 eV) at the room temperature. The results for the sample in Fig. 2 suggests the interpretation that the material exhibits another absorption edge at 1.05 eV. This value is only somewhat higher than those reported in [20]. However, to avoid uncertainty, a more suitable substrate than silicon should be used for this region of photon energies, because silicon has the fundamental absorption edge at 1.1 eV due to indirect transitions. Fig. 3 shows optical absorption spectra of β -$FeSi_2$ prepared onto a glass substrate measured at room temperature. The sample D without any influence of Si substrate exhibits the absorption edge near 1.05 eV, too.

The derivation of the reflection and transmission coefficients of the film-substrate system and the fitting procedure indicating how to obtain the index of refraction n and the extinction coefficient k (or the absorption coefficient $\alpha = 4\pi\nu k$, where ν is the wavenumber) from the reflectance and transmittance data were published elsewhere [21]. The index of refraction n and extinction coefficient k vs. photon wavenumber ν with the simulated spectral width of 20 cm^{-1} as calculated in [21] is shown in Fig. 4.

Fig. 5 shows the optical absorption spectra of the sample at different temperatures. An absorption is seen bellow the direct gap transitions. Although an indirect gap could explain a part of this absorption, an appreciable deal of it apparantly corresponds to the transitions between the defect levels within the forbidden gap and free carrier bands. These defect states are suspected to be present in our samples owing to the polycrystalline nature, non-stoichiometry or impurities.

The energy band gap of one our sample as a function of temperature is shown in Fig. 6. O'Donnell and Chen [22] obtained excellent fits with the experimental temperature dependences of the fundamental band gaps of Si, GaAs, GaP and C using

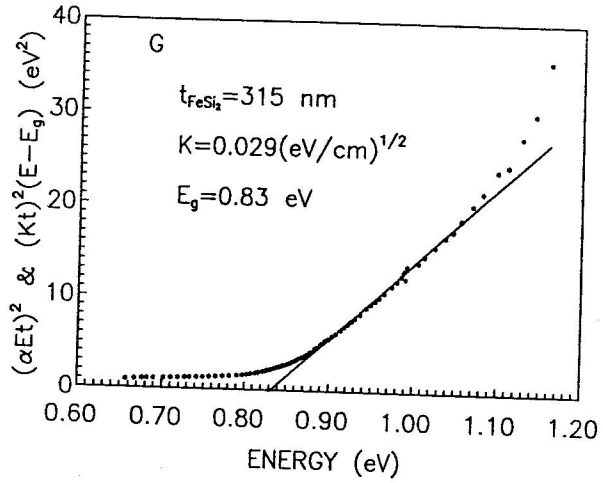

Fig. 2. Square of absorption coefficient times photon energy and β-$FeSi_2$ film thickness as a function of the photon energy for β-$FeSi_2$ thin film from Fig.1 at room temperature. The solid line indicates fit using Eq. 3.

the semiempirical expression

$$E_g(T) = E_g(0) - S\langle\hbar\omega\rangle\left[\coth\left(\frac{\langle\hbar\omega\rangle}{2kT}\right) - 1\right], \tag{4}$$

where $E_g(0)$ is the band gap at zero temperature, S is a dimensionlees coupling parameter, and $\langle\hbar\omega\rangle$ is the averaged phonon energy. The solid line in Fig. 6 is the calculated dependence according to the expression (4). The best fitting values of the parameters $E_g(0)$, S, and $\langle\hbar\omega\rangle$ together with their standard deviations (marked with symbol Δ in front of the corresponding parameter) are shown in Table 1. For comparison the values of Giannini et al. [11], Arushanov et al. [14], and Yang et al. [15] are also shown.

Comparison of the data shows that while $E_g(0)$ nearly coincides in all cases the other two parameters exhibit significant scatter in the values. Our averaged S is more than three times smaller than that of Giannini et al. [11], although a little smaller than but still comparable with the value of Arushanov et al. [14] and even better with the value of Yang et al. [15]. Our values of the coupling parameter can be compared to the reported values for silicon ($S = 1.49$) and diamond ($S = 2.31$) but they are smaller than those of GaAs ($S = 3.00$) and GaP ($S = 3.35$) [22].

At high temperatures, $T \gg \langle\hbar\omega\rangle$ the slope of E_g vs T approaches the value

$$\left(\frac{dE_g}{dT}\right)_{\max} = -2kS. \tag{5}$$

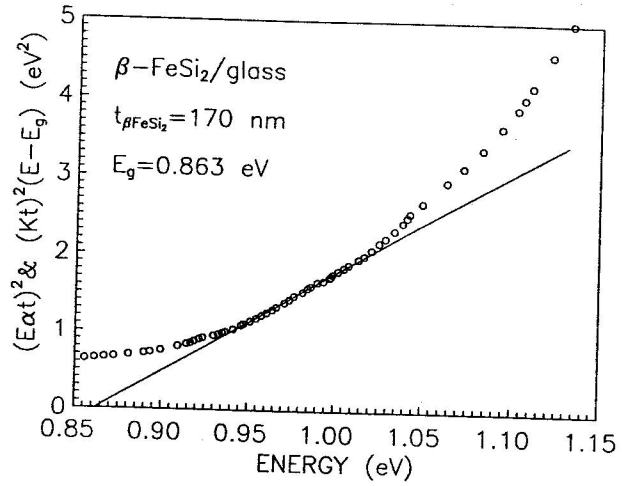

Fig. 3. Square of absorption coefficient times photon energy as a function of the photon energy for β-$FeSi_2$ thin film on glass at room temperature. The solid line indicates fit using Eq. 3.

$E_g(0)$ (eV)	$\Delta E_g(0)$ (eV)	S	ΔS	$\langle\hbar\omega\rangle$ (meV)	$\Delta\langle\hbar\omega\rangle$ (meV)	Ref. or Sample
0.900		6.22		71		[11]
0.894		2.75	0.25	55	3	[14]
0.901		2.15		34.5		[15]
0.891	0.0114	2.63	0.41	21.5	12.8	A
0.894	0.0015	1.88	0.22	46.8	6.5	B
0.897	0.0007	1.43	0.28	71	9.2	C
0.899	0.0012	2.11	0.16	44.7	4.4	D
0.895	0.0037	2.01	0.27	46.0	8.17	Ave. of A to D

Tab. 1. Fit parameters for temperature dependence of the direct band gap of β-$FeSi_2$

The calculated slope of E_g vs T with the average value of S equals -0.35 meV/K. This is the smallest published value. Giannini et al. [11] determined the highest value equal to -1.2 meV/K and the value published by Arushanov et al. [14] -0.48 meV/K is near to the earlier value determined by Waldecker, Meinhold and Birkholz [13] as -0.45 meV/K at high temperatures 700-1200 K.

The discrepancies can be explained by the fact that Giannini et al. [11] used polycrystalline films whereas Arushanov et al. [14] used single crystals. The polycrystalline samples could be influenced in particular by the defect levels, probably located at grain

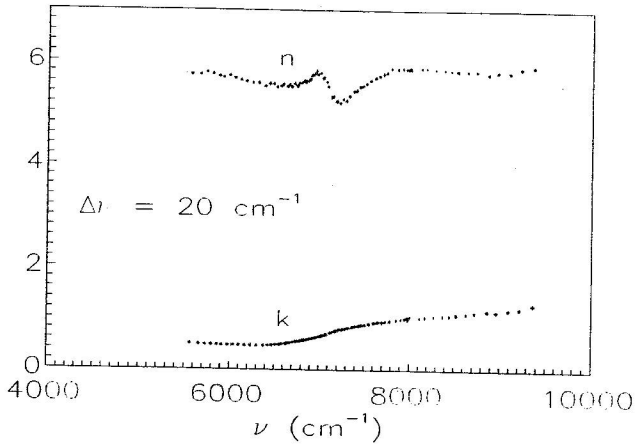

Fig. 4. Index of refraction n and extinction coefficient k vs. photon wavenumber ν for β-iron disilicide layer as calculated in [21] using equations for the reflectance and transmittance of the thin film-substrate system. The value $\Delta\nu$ is the simulated spectral line width resolution of the apparatus.

boundaries. However, this does not explain the good agreement of the values of the slope of E_g vs T determined by Arushanov et al. for single crystals [14] and Waldecker, Meinhold and Birkholz for bulk polycrystalline samples [13]. Also our results and values of Yang et al. [15] are rather near to or lower than the monocrystalline values.

The differences in the parameters from sample to sample suggest some non-uniformity in the technological processes [23]. Taking into account the strong coupling of the band-edge states to the lattice, predicted by Christensen [9], partly explain this difference by the distortion of the lattice. The distortion can be due to the strain or different chemical composition (nonstoichiometry) of the film and due to the different thermal expansion coefficient of the silicon (2.6×10^{-6}/K at room temperature) substrate and the silicide (6.7×10^{-6}/K [19]) layer. O'Donnell and Chen [22] showed that the dependence of band gap on lattice thermal expansion takes nearly the same analytical form as for the electron-phonon interaction. Therefore, equation (4) describes both lattice and phonon contributions to the band-gap shifts with temperature.

The great discrepancies in the phonon average energy suggest that it does not reflect only the bulk properties but also the effect of inter-grain material.

The mobility of carriers can be estimated using equation (5) in [11] assuming the same effective masses and the same coupling parameter for both electrons and holes. The low carrier mobility in β-$FeSi_2$ was predicted by Christensen [9] and attributed to a particularly strong electron-phonon scattering in the band-edge states. An obvious

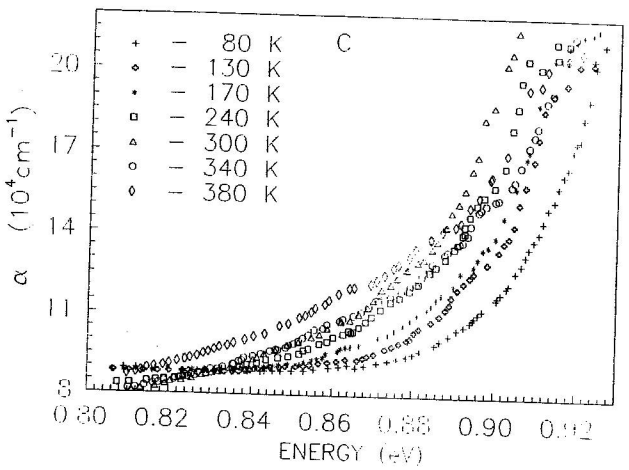

Fig. 5. Absorption spectra of the system β-$FeSi_2$/Si at different temperatures.

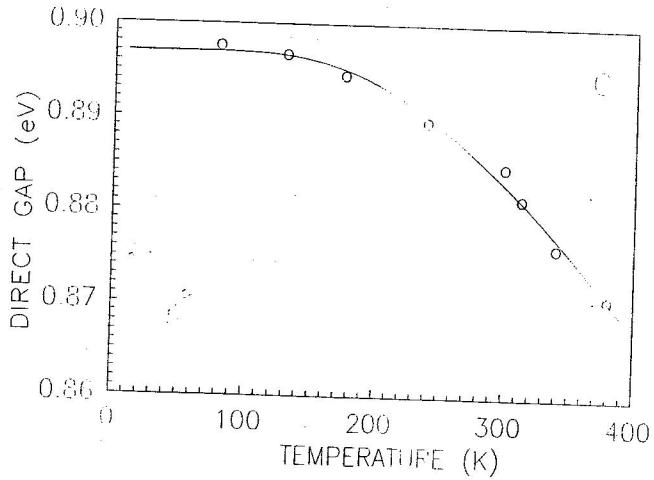

Fig. 6. The direct band gap as a function of temperature. The circles represent the experimental values of E_g and solid line is the calculated dependence according to Eq. 4.

discrepancy can be found for all the reported mobilities in β-$FeSi_2$. Electron mobilities at room temperature as low as 0.2 cm^2/Vs [1] and hole mobilities as high as 104 cm^2/Vs [12] have been measured. The latter value is much higher than the calculated mobility using the obtained values of S and $\langle\hbar\omega\rangle$. This indicates that the electron-phonon interaction may also vary with samples fabricated in different ways.

4 Conclusions

The optical properties of the β-iron disilicide semiconducting phase, prepared with a-Si or SiO_x capping overlayers without using ultrahigh vacuum processes were studied thoroughly. Our samples were investigated by optical transmittance measurements at temperatures betwen 80 and 380 K. The analysis of the optical absorption coefficient determined from the transmittance and reflectance measurements clearly favours the direct allowed transitions with the average forbidden energy gap $E_g = (0.87 \pm 0.04)$ eV at the room temperature. The relatively high differences in E_g for different samples are proposed to be due to the strong dependence of the band-edge states on the lattice distortion. There have been indications that the second energy absorption edge appears at 1.05 eV (Fig.2,3) which is in agreement with previous publications [25]. Analyzing the temperature dependence of the direct energy-gaps by means of the three-parameter thermodynamic model [22] has allowed us to find the following best fitting parameters: the band gap (at 0 K) 0.895 ± 0.0037 eV, the dimensionless lattice coupling parameter $S = 2.01 \pm 0.27$, and average phonon energy 46.0 ± 8.17 eV. Unlike the theoretical prediction [9] and the earlier reported result [11], our results do not show any evidence of a particularly strong electron-phonon interaction which would give lower carrier mobilities. By examining all reported triplets of parameters for β-$FeSi_2$ fabricated by different techniques and thermal processes, an obvious discrepancy can be found for the lattice coupling parameter S and the average phonon energy $\langle\hbar\omega\rangle$, although the band gaps at 0 K are very similar. Our parameters are near to the values previously published for the single-crystal silicide [14] and the ion beam synthesized polycrystalline layer [15].

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