Infrared spectra of semiconducting silicides nanolayers

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Abstract. The infrared absorption is studied of samples consisting of a Si matrix with unburied nanolayers of the semiconducting silicides $\beta$-FeSi$_2$ and MgSi. Features additional to those due to the transversal optical phonon s of the compounds are observed. The features are interpreted in the framework of the appearance of surface and interface phonon polaritons, which absorb the light. Insofar as the frequencies of the longitudinal optical (LO) phonon-polariton modes are close to those of the LO phonon frequencies, the infrared transmittance of nanolayers can be regarded as a method for direct determination of these frequencies.

1. Introduction
The advance in fabrication of new optical devices based on low-dimensional systems where the interface properties often become dominant has enhanced the interest in studying the interface modes of the elementary excitations and, in particular, of the surface and interface phonon-polaritons (SPP and IPP). The SPP and IPP modes can be also detected by measuring the infrared transmission. The purpose of the work is to obtain the LO phonon frequencies of the semiconducting silicide $\beta$-FeSi$_2$ which has not been reported so far.

2. Sample preparation and characterization
1. Samples with MgSi$_2$ layers: The implantation of $^{24}$Mg$^+$ ions with a dose of $4\times10^{17}$ cm$^{-2}$ was performed at an of energy $E_i = 40$ keV into n-type (100)Si wafers. After implantation the samples were annealed at a temperature of $T_a = 500$ °C for different annealing times of $t_a = 30$ s (s. 41) and $t_a = 60$ s (s. 42). The cross-section of the samples was characterized by high resolution TEM (HR-XTEM). The TEM images of the samples showed that the MgSi$_2$ layers thickness varies from 160 to 220 nm due to the formation of grains with different sizes, as can be seen in figure 1.

2. Samples with $\beta$–FeSi$_2$ layers: Two types of samples were studied. The first one (s. 15) was produced by a two-step implantation process of $^{56}$Fe$^+$ ions with a dose of $5\times10^{16}$ cm$^{-2}$ at each step. $E_i$ was 60 keV at the first step and 20 keV at the second one. The implanted samples were annealed at $T_a = 900$°C for $t_a = 90$ s. The HR-XTEM overview images of the samples showed the formation of a relatively thin continuous polycrystalline $\beta$-FeSi$_2$ layer consisting of crystallites with different sizes and orientations leading to the formation of a rough surface, figure 2. The second sample (s. 42) was produced by $^{56}$Fe$^+$ ion implantation with a dose of $1\times10^{17}$ cm$^{-2}$ and an energy of 25 keV in a first step and with a dose of $4\times10^{17}$ cm$^{-2}$ and an energy of 90 keV in the second one. The rapid thermal
Annealing was first performed at $T_a = 800^\circ C$ for $t_a = 15$ s and then at $T_a = 900^\circ C$ for $t_a = 60$ s. R.m.s. surface roughness of about 60 nm was observed by atomic force microscopy [1].

![Figure 1. HR-XTEM image of the s. 41.](image1)

![Figure 2. HR-XTEM image of the s. 15.](image2)

3. Experimental results

The IR transmittance spectra of the samples were taken at 300 K using a Bohmem Fourier spectrometer and are shown for MgSi$_2$ layers in figure 3 and for $\beta$–FeSi$_2$ layers in figure 4.

![Figure 3. IR transmittance spectra of samples s. 41 and s. 42 with Mg$_2$Si layers. The Raman spectrum of s. 41 is given for comparison.](image3)

![Figure 4. IR transmittance spectra of samples s. 15 and s. 42 with $\beta$–FeSi$_2$ layers. The Raman spectrum of s. 15 is given for comparison.](image4)

The frequency of the well-observed minima in the IR spectra of s. 41 and s. 42 at 272 cm$^{-1}$ coincides fairly well with those obtained by theoretical and other experimental investigations [2, 3] for the single IR active mode of cubic Mg$_2$Si.
The main features in the IR spectra of the orthorhombic $\beta$-FeSi$_2$ with a cell containing 48 atoms originate from the motion of Fe and Si atoms [4] and are positioned at the following frequencies: at 308 cm$^{-1}$, at about 345 cm$^{-1}$ and 383 cm$^{-1}$ along the $a$-axis; at 324 cm$^{-1}$, at a frequency slightly higher than 345 cm$^{-1}$ and at about 397 cm$^{-1}$ along the $b$-axis; at 303 cm$^{-1}$, at a frequency slightly higher than 345 cm$^{-1}$ and at about 382 cm$^{-1}$ along the $c$-axis. The features detected at 267 cm$^{-1}$ ($a$-axis), 293 cm$^{-1}$ ($b$-axis) and 276 cm$^{-1}$ ($c$-axis), are related to the motion of the Fe-Fe atoms. Those in the range about 400-430 cm$^{-1}$ are attributed to the Si-Si atom motion. All these features, marked in figure 4, are detected in the IR spectra of s. 15 and s. 42.

In the spectra of both types of samples additional features can be resolved. The additional features in the Raman spectra of these samples, given for comparison with the IR spectra in figure 3 and figure 4, were attributed to SPP and IPP modes, which take place at the surface and interface of the thin silicide layers [5].

4. Discussion

It was shown [6] that on the surface and interface of thin layers the SPP and IPP modes not only scatter but also absorb the light. The absorption bands in the vicinity of the LO phonon frequencies have been observed in thin layers at incident angles $\theta > 0$ [7]. The comprehensive theoretical investigations [6] show that in general three absorption peaks are expected in the absorption spectrum of a phonon mode. The first one, related to the polariton mode of the LO-phonon, is situated close to the frequency of the LO mode $\omega_{LO}$ and has the highest absorption, proportional to $k d \sin^2 \theta$ ($k$ is the wave-vector, $d$- the film thickness and $\theta$ - the incident light angle). The mode interacts only with the parallel component of the electro-magnetic field of the light. The light is absorbed also by the TO mode at the frequency $\omega_{TO}$ of this mode. The third absorption peak is related to the polariton mode of the TO phonon mode. Its frequency is close to $\omega_{TO}$ and these two peaks overlap in the case of very thin films.

In the IR spectra of the samples with Mg$_2$Si layers three absorption bands are clearly observed, one at 275 cm$^{-1}$, due to the TO mode, the second close to the TO mode, due to the TO phonon polariton mode and the third at about 345 cm$^{-1}$, obviously related to the LO phonon polariton mode. The intensity of the last mode is not the highest, which is reasonable if one takes into account that the spectra are taken at normal incidence of light and the absorption should be attributed to the surface roughness.

The dispersion branches of SPP and IPP modes in the system air/$\beta$-FeSi$_2$/Si are calculated in the same way as those in the system air/Mg$_2$Si/Si. However, there is a number of TO phonons in $\beta$-FeSi$_2$.

The available value of $\omega_{LO} = 522$ cm$^{-1}$ for $\beta$-FeSi$_2$, published in [8], corresponds to $\omega_{TO} = 311$ cm$^{-1}$. It follows from the Lyddane-Sachs-Teller relation that the ratio between the static $\varepsilon_0$ and optical $\varepsilon_\infty$ dielectric functions along the $a$-axis is $\varepsilon_0 / \varepsilon_\infty = 2.75$. The values of all the TO frequencies are known. The surfaces of the samples with $\beta$-FeSi$_2$ layers are also rough. Therefore, the additional features in the IR spectra can be attributed to an absorption due to LO phonon polaritons modes with frequencies close to those of the corresponding LO phonon modes. Taking also into account the higher values of $\varepsilon_\infty$ along the $b$- ($\varepsilon_0 / \varepsilon_\infty = 2.67$) and $c$-axis ($\varepsilon_0 / \varepsilon_\infty = 2.49$) and in accordance with the experimental IR spectrum at higher frequencies, the values of the remaining LO modes were obtained. Figure 5 shows a mapping of six sets of dispersion relations for the more intense TO modes calculated for a $\beta$-FeSi$_2$ layer with a thickness of 40 nm. The corresponding frequencies $\omega_{TO}$ and $\omega_{LO}$ are listed in the figure.

The additional features in the IR spectra at higher frequencies are attributed to the LO phonon-polariton modes. The frequencies of the LO phonon-polariton modes $\omega_{LO}$ are close to those of the compound, as can be seen from the dispersion relations. Then the $\beta$-FeSi$_2$ LO phonons, not reported up to now, are evaluated. The features due to the absorption of the TO phonon-polariton modes
obviously contribute to the broadening of the TO phonon mode features and cannot be clearly resolved. According to the theory, the absorption due to the LO phonon-polariton modes at normal incidence must be zero, as far as it is proportional to $\sin^2 \theta$. The presence of features in the IR spectra, although of low intensity, must then be attributed to the surface roughness.

5. Conclusions
The investigation of the IR spectra of materials in the form of nanolayers where SPP and IPP modes can be excited appears to be a method for the direct determination of the LO phonon frequencies of materials. The frequencies of the $\beta$-FeSi$_2$ LO phonons, not reported up to now, have been evaluated.

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