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# Surface and Interface Polaritons of the Optical Phonons in $Mg_2Si$ Nanolayers with Rough Surfaces

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**Abstract.** Nanolayers of $Mg_2Si$, embedded into $Si$ matrix by ion-beam synthesis are studied. The layers are prepared with the same dose of the implanted $Mg$ ions but with different energies of implantation and thus they are formed at different depth in the matrix. The surface of the samples is studied by atomic force microscopy (AFM) and the roughness height is determined. Raman scattering spectra of the samples are obtained and along with the characteristic $Mg_2Si$ phonon modes additional features are observed. These features are assigned to generation of surface and interface phonon-polariton modes. The samples are considered as a four-layered structure. The dispersion relations of the polariton modes are calculated from the boundary condition for a continuity of the polariton electric field. The features in the spectra are interpreted on the base of the calculated dispersion relations and the role of the surface roughness is evaluated.

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## 1 Introduction

The physical properties of low-dimension structures differ from those of the bulk materials. In particular new phonon and electronic excitations appear. The influence of the interface strongly increases when embedding nanostructures in a matrix. The interface phenomena often became dominant.

It is known that when a thin layer of an active material, medium with a negative dielectric function in a certain frequency region, is placed on a substrate with higher dielectric constant in the same region, branches of surface-phonon polariton (SPP) and interface-phonon polariton (IPP) modes can be generated. The investigation of the interface and surface excitation modes gives information about the size of the embedded nanoformations and the quality of the interface

between the material and the matrix. This allows the evolution of nanoformations by the change of the preparation conditions to be followed.

In our previous investigations [1, 2] the additional features in the Raman spectra of $Mg_2Si$ embedded into Si matrix by ion-beam synthesis are assigned to generation of SPP and IPP modes. In samples with significant roughness, features additional to the predicted from the polariton dispersion relations, calculated for a flat surface, are observed.

In the paper the phonon-polariton dispersion relations are calculated considering the roughness as a layer with an effective dielectric function. The calculations predict generation of additional excitations. The results are compared with the experimental Raman scattering spectra.

## 2 Samples Preparation and Experiment

The samples were prepared by ion-beam synthesis, followed by rapid thermal annealing. The mass-separated $^{24}Mg^+$ ions were implanted into (001) Si wafers. The dose of the implanted Mg ions was $8 \times 10^{17}$ cm$^2$. The implantation was performed with two different energies: 40 keV (s. 127) and 60 keV (s. 147). The annealing temperature and the time duration for both types of samples were the same: $500°$C and 300 s. The peak concentration in the samples, implanted at lower energy, is placed closer to the sample surface.

The micro-Raman spectra in the range between 150 and 700 cm$^{-1}$ were measured at room temperature using a triple multichannel spectrometer, Microdil 28 (Dilor), equipped with an optical microscope (objective $\times 100$; NA = 0.95) for focusing the incident laser beam ($Ar^+$ laser; $\lambda = 488.0$ nm; $P_L \approx 13$ mW on the sample; focus spot diameter about 2–3 $\mu m$). The scattered light was collected in the near backward-scattering geometry (A). The unpolarized Raman spectra in near $90°$ scattering configuration (B) were studied using SPEX 1403 double spectrometer equipped with photomultiplier working in a photon counting mode. The spectra were taken with spatial slit width of 4 cm$^{-1}$ and accumulated with frequency step of 1 cm$^{-1}$. The semiconductor $Mg_2Si$ belongs to the cubic system with space group $Fm\overline{3}m(Oh^5)$. The material has three atoms in the primitive unit cell and therefore six optical branches in the vibrational dispersion curves at the center of the Brillouin zone are allowed. According to factor-group analysis the optical phonon modes with wave vector $k \approx 0$ are triply degenerated and correspond to $F_{2g}$ and $F_{1u}$ irreducible representations. Because of the inversion symmetry, the $F_{2g}$ and $F_{1u}$ modes are Raman-active and infrared-active, respectively. Due to the macroscopic electric field the $F_{1u}$ mode splits into a doubly degenerated TO mode and a LO mode. The theoretical calculations give for the frequency of the triply degenerated Raman- allowed $F_{2g}$ mode the value 258 cm$^{-1}$ [3, 4]. Another sharp line, assigned to Fröhlich-interaction-induced scattering by Raman-inactive $F_{1u}$(LO)-mode, is usually ob-

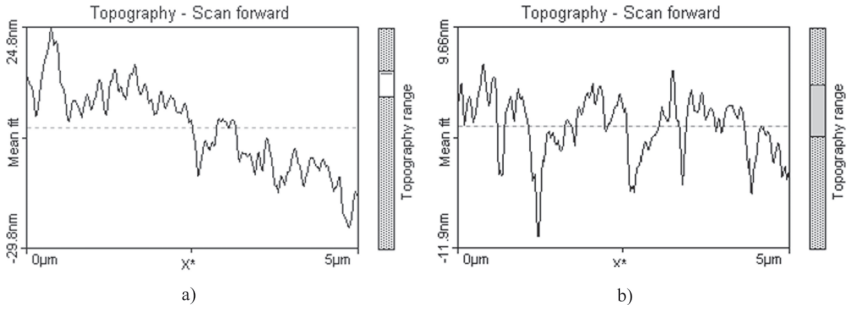


Figure 1. Topography of the surface roughness of: a) s. 127 and b) s. 147, studied by AFM (easyScan2 AFM, Nanosurf, CH)

served at 348 $cm^{-1}$ in the Raman spectra of $Mg_2Si$ [5–8]. Thus, the peaks at 256 $cm^{-1}$ and 258 $cm^{-1}$, observed in our experimental spectra, are related to the $F_{2g}$ and $F_{1u}$ (LO) modes of the $Mg_2Si$.

The atomic force microscopy (AFM) investigations (easyScan2 AFM, Nanosurf, CH) (Figure 1) shows that the surfaces of the samples s. 127 and s. 147 are rough and the roughness height is about 50 nm and 20 nm, respectively. The later is in coincidence with the earlier finding [7] that in the samples implanted with lower energy (s. 127) and thus with a peak Mg concentration closer to the surface, the formation of dendrites is more intense than in the sample implanted with higher energy, s. 147. The thickness of the continuous $Mg_2Si$ layer in s. 127 is about 200 nm and about 400 nm in s. 147.

## 3 Dispersion Relations

The asymmetry of the Raman peaks, appearing in the frequency range between the $Mg_2Si$ TO and LO phonon frequencies, where the dielectric function is negative, implies undoubtedly the appearance of SPP and IPP modes. In order to interpret the experimental Raman spectra, the polaritons dispersion relations were obtained as solutions of the Maxwell's equations, written for a certain number of contacting media. The dispersion relations in the system air/$Mg_2Si$/Si were calculated following the way proposed by Mills and Maradudin [9] in the assumption of isotropic media and light velocity $c \rightarrow \infty$, from the boundary conditions and we get the formula:

$$[1+\varepsilon_1(\omega)]\Big[1+\frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)}\Big]-\exp(-2kd_1)[1-\varepsilon(\omega)]\Big[1-\frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)}\Big]=0, \qquad (1)$$

where $\varepsilon_1(\omega)=\varepsilon_{i\infty}\dfrac{\omega_{i\mathrm{LO}}^2-\omega^2}{\omega_{i\mathrm{TO}}^2-\omega^2}$ are the dielectric functions of $Mg_2Si$ ($i=1$) and Si ($i=2$), $d_1$ is the thickness of the $Mg_2Si$ layer. The values $\omega_{i\mathrm{TO}}$ and $\omega_{i\mathrm{LO}}$

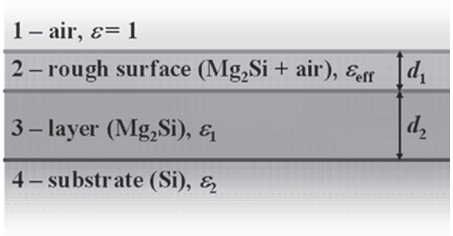


Figure 2. A scheme of the four layer structure used for calculation of the phonon-polariton dispersion relations.

of $Mg_2Si$ are not only theoretically predicted, but experimentally established [6,10]. The values of the optical dielectric functions of $Mg_2Si$ and Si are known: $\varepsilon_{1\infty} = 13.3$ and $\varepsilon_{2\infty} = 11$, respectively.

To evaluate the influence of the roughness we consider four-layered structure, shown in Figure 2. The rough surface is considered as a layer with an effective dielectric function, $\varepsilon_{\text{eff}}$. In our case the shape of the roughness is not defined. Thus in order to obtain $\varepsilon_{\text{eff}}$ we used the extended Maxwell-Garnett formula for non-spherical shape of the pores [11], namely:

$$\varepsilon_{\text{eff}}(\omega) = \varepsilon_1(\omega)\Big[1 + (1-x)\frac{1-(\varepsilon_1(\omega)}{\varepsilon_1(\omega) + xf(1-\varepsilon_1(\omega))}\Big]. \qquad (2)$$

Here $x$ is the volume fraction of the crystal and $f$ is depolarization factor. The evaluations from the AFM data give the value 0.5 for $x$. The depolarization factor depends on the pores shape. The shape of pores in our case more suitable can be regarded as thin rods, for which the value 0.5 is given [12].

For four-layered structure we obtain the following formula for the dispersion relations of SPP and IPP phonon-polariton modes:

$$\Big(1+\frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)}\Big)\Big[(1+\varepsilon_{\text{eff}}(\omega))\Big(1+\frac{\varepsilon_{\text{eff}}(\omega)}{\varepsilon_1(\omega)}\Big)-\exp(-2kd_1)(1-\varepsilon_{\text{eff}}(\omega))\Big(1-\frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)}\Big)\Big]$$
$$+\exp(-2kd_2)\Big(1-\frac{\varepsilon_1(\omega)}{\varepsilon_2(\omega)}\Big)\Big[1-\frac{\varepsilon_{\text{eff}}(\omega)}{\varepsilon_1(\omega)}\Big(1+\varepsilon_{\text{eff}}(\omega)\Big)$$
$$-\exp(-2kd_1)\Big(1+\frac{\varepsilon_{\text{eff}}(\omega)}{\varepsilon_1(\omega)}\Big)(1-\varepsilon_{\text{eff}}(\omega)\Big] = 0, \quad (3)$$

where $d_1$ is the thickness of the rough surface and $d_2$ is the thickness of the continuous $Mg_2Si$ layer.

The numerical solutions of equation (3), calculated with the corresponding thicknesses of the porous and continuous layers of s. 127 ($d_1 = 50$ nm and $d_2 = 200$ nm) (dash lines) and s. 147 ($d_1 = 20$ nm and $d_2 = 400$ nm) (dash-dot lines) give the theoretical dispersion relations, shown in Figure 3. In Figure 3

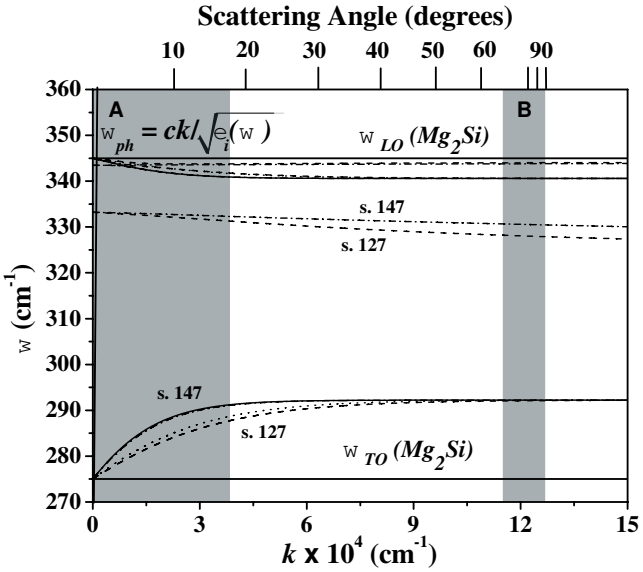


Figure 3. Calculated phonon-polariton dispersion relations for s. 127: four-layered structure (dash lines) with roughness height $d_1 = 50$ nm and continuous layer thickness $d_2 = 200$ nm and three-layered structure (dot lines) – continuous layer $Mg_2Si$ 250 nm; for s. 147: four-layered structure (dash-dot lines) with roughness height $d_1 = 20$ nm and continuous layer thickness $d_2 = 400$ nm and three-layered structure (thin black solid lines) - continuous layer $Mg_2Si$ 420 nm. The range of the wave-vectors in scattering geometry A and B are shadowed.

the calculations are compared with those for a three-layered structure, air/$Mg_2Si$ continuous layer/Si. The dot lines represent the results for $d_{Mg_2Si} = 250$ nm (s. 127) and the thin black solid lines – the relations for $d_{Mg_2Si} = 420$ nm (s. 147). The frequencies of TO and LO phonon modes of $Mg_2Si$ are marked as thick black lines in Figure 3. The photon dispersion relations, to the right of the line $\omega_{ph} = ck\sqrt{\varepsilon_i(\omega)}$, which limits the existence of polariton modes, are shown in Figure 3, as well.

## 4 Results and Discussion

The experimental Raman spectra obtained in both scattering configurations, A and B, are shown in Figure 4 for both samples.

The characteristic $Mg_2Si$ peaks in the Raman spectra are at about 256 $cm^{-1}$ and 345 $cm^{-1}$, assigned to $F_{2g}$ and LO $F_{1u}$ phonon modes, respectively. Along with these lines additional features in the spectra are observed. The most pronounced features consist in a broadening and an asymmetry of the LO lines in the spectra,

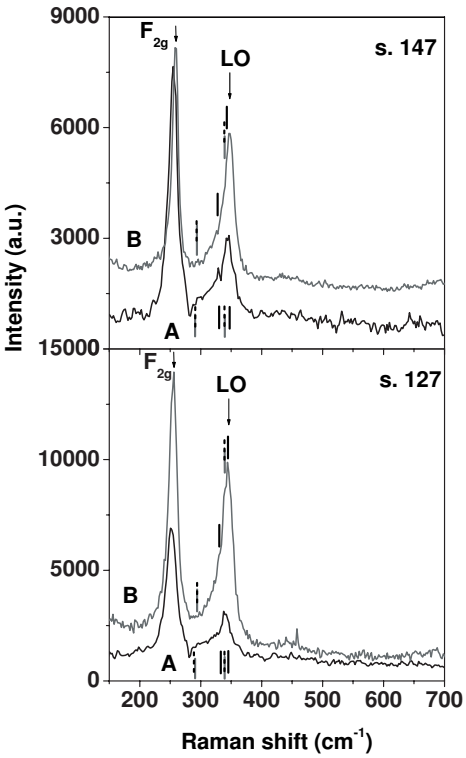


Figure 4. Raman spectra, taken in the two scattering configurations – A (black) and B (grey) – for s. 127 and s. 147. The frequencies of the predicted from the dispersion relations phonon-polariton modes are marked with grey bars in the case of three-layered structures, with black bars – the additional phonon-polariton modes in the case of four-layered structure and with dot black bars – the $Mg_2Si$ TO and $Mg_2Si$ LO phonon-polariton modes in the case of four-layered structure.

which is more significant in the spectra obtained in A scattering configuration.

For the three-layered structure three branches of phonon polariton modes, two of them in the $Mg_2Si$ layer and one in the Si substrate, propagate. The mode, propagating in Si, with much higher frequency, is not shown in Figure 3. For the $Mg_2Si$ layer with thickness 250 nm the frequencies of the modes have to be expected at 290 and 341.7 $cm^{-1}$ for scattering configuration A and at 292 and 340.7 $cm^{-1}$ for configuration B. For $Mg_2Si$ layer with a thickness of the 420 nm these frequencies have to be expected at 291 and 341 $cm^{-1}$ for scattering configuration A, and at 292 and 340.7 $cm^{-1}$ for configuration B. The mentioned frequencies are marked in Figure 4 with grey bars.

The main difference in the dispersion relations of the three- and four-layered

structures consists in the generation of two additional branches, propagating in the porous layer: at 332 and 343.7 $cm^{-1}$ (A – configuration) and at 331.5 and 343.7 $cm^{-1}$ (B – configuration) for s. 127 and at 331.5 and 343.7 $cm^{-1}$ (A – configuration) and at 328 and 344 $cm^{-1}$ (B – configuration) for s. 147. Features, related to these modes, are well seen in the Raman spectra, Figure 4 (black bars).

The influence of the roughness on the polariton modes, propagating in the continuous $Mg_2Si$ layer consists in a shift of the mode frequencies to the lower ones (dotted black bars in Figure 4). The shift depends on the ratio of the thicknesses of the porous and the continuous layers. Thus it is much more pronounced in the sample with the thinner continuous layer, s. 127, and reaches 3 $cm^{-1}$ for the TO phonon modes.

## 5 Conclusion

The frequencies of SPP and IPP modes observed in the Raman spectra of the samples representing $Mg_2Si$ nanolayers embedded in Si matrix are calculated, taking into account the roughness of the sample surface considering the samples as four-layered systems air/$Mg_2Si$+air/$Mg_2Si$/Si. The accounting for the surface roughness leads to:

(i) the generation of two additional phonon-polariton modes in comparison to three-layered system air/$Mg_2Si$/Si;

(ii) a shift of the modes frequencies of the polaritons propagating in the continuous $Mg_2Si$ layer to the lower frequencies. The shift is more pronounced for the TO phonon-polariton modes and depends on the ratio of the porous and continuous layers thicknesses.

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