Polariton modes in ion-beam synthesized Mg$_2$Si nanolayers

M Baleva $^1$, G Zlateva $^2$, A Atanassov $^1$, M Marinova $^3$ and E Polychroniadis $^3$

$^1$Faculty of Physics, St. Kl. Ohridski University of Sofia, 5 J. Bourchier Blvd., 1164 Sofia, Bulgaria
$^2$Faculty of Medicine, St. Kl. Ohridski University of Sofia, 1 Koziak Str., 1407 Sofia, Bulgaria
$^3$Solid State Physics Section, Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

E-mail: baleva@phys.uni-sofia.bg

Abstract. Micro-Raman scattering of a Si matrix with Mg$_2$Si nanolayers on it is studied. The samples are prepared by ion-beam synthesis followed by rapid thermal annealing. We succeeded in measuring Raman scattering by surface and interface phonon polaritons. The experimental results are interpreted on the basis of the dispersion relations calculated for layers with different thickness. The shift of the polariton modes from sample to sample is in agreement with the variation of the nanolayer’s thickness.

1. Introduction

The advances in nanotechnology and nanoscience renewed the interest in studying the interface modes of elementary excitation processes. In a matrix with nanoformations the interface properties often become dominant. The interface phonon modes lie between longitudinal optical (LO) and transverse optical (TO) frequencies of the active media where the dielectric function is negative.

We used Raman scattering to study samples consisting of a Si matrix with unburied Mg$_2$Si nanolayers formed by ion beam synthesis (IBS). The compound Mg$_2$Si is one of the dozen semiconducting metal silicides. The interest in studying these materials stems mainly from the fact that they are non-toxic and inexpensive. We obtained micro-Raman spectra in near backscattering geometry. The asymmetry in the Raman mode peaks is associated with the appearance of surface-phonon polariton (SPP) and interface-phonon polariton (IPP) modes. The theoretical dispersion relations of the SPP and IPP modes in the system air/Mg$_2$Si/Si for different thicknesses of the Mg$_2$Si nanolayer are obtained from the Maxwell equations, following the procedure used by Mills and Maradudin [1].

2. Sample preparation and characterization

The samples were prepared by IBS followed by rapid thermal annealing. The IBS process was chosen for the following reasons: i. The oxidation of Mg implanted into the Si matrix can be avoided to a great extent; ii. The formation of thin Mg$_2$Si films by conventional preparation techniques is restricted because of the low condensation coefficient and high vapor pressure of Mg [2]. The limitations of the standard thin film preparation techniques can be avoided by using the IBS method; we succeeded in growing Mg$_2$Si layers with a thickness of about several hundred nanometers. The formation of Mg$_2$Si in our IBS prepared samples was proved by infrared (IR) transmittance and Raman scattering. The
characteristic infrared active phonon mode at 276 cm\(^{-1}\) alone has been recently detected in the IR transmittance spectra \[3\]. The Raman peak due to the triply degenerated allowed F\(_{2g}\) Raman mode at 256 cm\(^{-1}\) as well as the sharp line assigned to Fröhlich-interaction-induced Raman-inactive longitudinal optical (LO) mode (split from the F\(_{1u}\) mode) at 345 cm\(^{-1}\) have been also observed in the Raman spectra of ion beam synthesized Mg\(_2\)Si samples \[4\]. Here the results are given of the study of samples prepared with the same implantation dose of 4\(\times\)10\(^{17}\) cm\(^{-2}\) and different implantation energies, namely, \(E_i = 40\) keV (sample s41) and \(E = 60\) keV (sample s73). After the implantation the samples were annealed at the same temperature of 500°C, for 30 s (s. 41) and 300 s (s. 73).

The morphology of the samples was studied by cross-sectional transmission electron microscopy (XTEM). The TEM observations were performed on a JEM 100CX TEM working at 100 kV. The overview images of the two types of samples are shown in figure 1 and figure 2. The surface of the Mg\(_2\)Si layer in the sample prepared with lower \(E_i\) (s. 41) is rough because of a dendritic silicide growth as reported earlier \[5\]. The thickness of the dendrite region is of the order of 70 nm and is followed by a region of a dense layer with a thickness of approximately 160 nm. The Mg\(_2\)Si layer in the sample prepared with higher \(E_i\) (s. 73) shows a relatively uniform thickness of 190 nm.

3. Experimental results
The micro-Raman spectra were measured by a triple multichannel spectrometer Microdil 28 (Dilor) equipped with an optical microscope (objective \(\times 100\) and numerical aperture (NA) = 0.95). An Ar\(^+\) laser (wavelength \(\lambda = 488.0\) nm, power \(P_L \approx 10\) mW, focus spot diameter about 2 \(\mu m\)) was used for excitation. The unpolarized micro-Raman spectra taken in a backscattering geometry are shown in figure 3 and figure 4. Along with the Raman peaks due to the F\(_{2g}\) and the LO modes, an apparent asymmetry of the peaks as well as a broad feature at about 450 cm\(^{-1}\) are seen in the spectra. In the geometry used the scattering angle \(\theta\) varies from 0° to about 17°. The corresponding range of the wave-vector, shadowed in figure 5, (from 0 to about 4\(\times\)10\(^4\) cm\(^{-1}\)) was calculated according to the relation \(k = k_i \sin \theta\) (\(k_i = 12.9 \times 10^4\) cm\(^{-1}\)), where \(k_i\) is the incident light wave-vector.

The densities of the polariton states for layers with thicknesses 50, 150 and 400 nm are shown below the spectrum.
4. Discussion
The asymmetry of the Raman peaks appearing in the frequency range between the Mg$_2$Si TO and LO phonon frequencies, where the dielectric function is negative, implies the appearance of SPP and IPP modes. The dispersion relations in the system air/Mg$_2$Si/Si are calculated following the procedure proposed by Mills and Maradudin [1]. Assuming an isotropic media and light velocity $c \rightarrow \infty$, and using the boundary condition for continuity of the polariton electric field, we obtain the following dispersion relation:

$$
\left[1 + \varepsilon_2(\omega)\right] \left[1 + \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)}\right] - \exp(-2kd_2) \left[1 - \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)}\right] \left[1 - \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)}\right] = 0.
$$

The equation is frequency dependent only through the quantities $\varepsilon_i(\omega)$, with $i = 1$ for Si and 2 for Mg$_2$Si, and can be solved numerically. In the relations, $d$ is the layer thickness, the dielectric function $\varepsilon_i(\omega)$ can be written in terms of measurable quantities $\varepsilon_i(\omega) = \varepsilon_{\infty}(\omega_{\text{LO}}^2 - \omega^2)/(\omega_{\text{TO}}^2 - \omega^2)$, where $\omega_{\text{LO}}$ and $\omega_{\text{TO}}$ are LO and TO phonon frequencies, respectively, and $\varepsilon_{\infty}$ are the optical dielectric functions. The numerical solution of equation (1) gives the theoretical dispersion relations shown in figure 5 for different thicknesses of the Mg$_2$Si layer.

The values $\omega_{\text{TO}}$ and $\omega_{\text{LO}}$ of Mg$_2$Si are not only theoretically predicted, but experimentally established [3, 4]. The value of the optical dielectric function $\varepsilon_{\infty} = 12.25$ is known as well [6]. Although the optical phonons in covalent semiconductors, such as Si, are not IR active, they absorb the light. The identifications of the peaks in the IR absorption spectra of Si based on the assumption that these peaks involve sums and differences of four zone-edge phonon frequencies in the transverse acoustic (TA), longitudinal acoustic (LA), TO and LO phonon branches gives $\omega_{\text{LA}} = 128$ cm$^{-1}$; $\omega_{\text{TA}} = 340$ cm$^{-1}$; $\omega_{\text{TO}} = 482$ cm$^{-1}$ and $\omega_{\text{LO}} = 414 \div 420$ cm$^{-1}$. Thus we used the following values for Si in the calculations: $\omega_{\text{TO}} = 482$ cm$^{-1}$, $\omega_{\text{LO}} = 416$ cm$^{-1}$ and $\varepsilon_{\infty} = 10.09$.

The dispersion relations give two branches of polariton modes in the frequency region of the Mg$_2$Si optical phonons and one in the region of the Si ones. It is seen from figure 5 that as the layer thickness is decreased the polariton modes frequencies tend to the compound phonon mode frequencies. The density of states $g(\omega)$ of the polariton modes is calculated from each of the dispersion branches, obtained for the different thicknesses of the Mg$_2$Si layer. The density of states, as is well known, obeys the relation $g(\omega) \propto k^2 \frac{dk}{d\omega}$. The derivatives $\frac{dk}{d\omega}$ are numerically calculated from the dispersion branches, given in figure 5, in the whole range of wave vectors. The limitation of the $g(\omega)$ in the range of the scattering angles was performed by means of the Sigmoid function, which in our case has the form

$$
\Sigma(\omega) = \left[1 + \exp\left(\frac{d}{d\omega}\left(-\frac{d}{d\omega}\right)\right)\right]^{-1},
$$

where $\left(\frac{d}{d\omega}\right)$ is the value of the derivative at the corresponding boundary frequency and $\Delta \frac{dk}{d\omega}$ is the broadening parameter. The results are presented in figure 6.

In the sample implanted at the higher ion energy (s. 73), a Mg$_2$Si layer with a thickness of about 190 nm is formed. The densities of states for the three branches corresponding to a layer with a thickness of 200 nm are inserted in figure 4 below the Raman spectrum. It is seen that the positions of the additional features in the spectrum and the maxima in the densities of states coincide fairly well. In order to interpret the Raman spectrum of the sample prepared with the lower implantation energy (s. 41), one has to take into account the following: i. The thickness of the dendrite region varies from 0...
to about 70 nm. Therefore, the optical density of this surface layer is lower than that of the continuous layer below it and the layer can be regarded as a thinner dense layer; ii. The surface roughness leads to a strong increase of the scattering angle range. The later is identical to an increase of the layer thickness. Therefore it is reasonable to expect that apart from the continuous layer with thickness of about 160 nm, the contribution to the scattering of layers with thicknesses of about 50 nm and 400 nm must be taken into account. The densities of states for all three branches corresponding to layers with three different thicknesses – 50, 150 and 400 nm, are inserted in figure 3 below the Raman spectrum of s. 41. A good correspondence is seen in figure 3 and figure 4 between the positions of the additional features in the spectrum and the maxima in the densities of states. The much higher broadening of the features in the experimental spectra is reasonable if one takes into account that the layer thickness is not uniform and the roughness is statistically distributed.

5. Conclusions
A comparison is made of the calculated and experimentally obtained wave-number positions of the SPP and IPP modes in the system air/Mg$_2$Si/Si with different thickness of the Mg$_2$Si layer. It can be concluded that the investigation of the SPP and IPP modes appears to be a reliable method for the evaluation of the thickness of nanolayers and their morphology.

Acknowledgments
The work is supported by the National Scientific Fund at the Ministry of Education and Science of Republic of Bulgaria, contract number Ф1301/03, by Sofia University’s Fund for Scientific Investigations, contract number 1, and by the French-Bulgarian bilateral Program PAI-RILA 2/5.

References
[1] Mills D L and Maradudin A A 1973 Phys. Rev. Lett. 31 372
[2] Mahan J E, Vantomme, A Langouche G and Becker J 1996 Phys. Rev. B 54 16265
[3] Goranova E, Amov B, Baleva M, Trifonova E P and Jordanov P 2004 J. Matt. Sci. 39 1857
[4] Baleva M, Zlateva G, Atanassov A, Abrashev M and Goranova E 2005 Phys. Rev. B 72 115330
[5] Atanassov A, Zlateva G, Baleva M, Goranova E, Amov B, Angelov C and Mikli V 2006 Plasma Process. Polym. 3 219
[6] Vantome A and Langouche G 1996 Phys. Rev. B 54 11965