Studies of Raman Scattering from $Bi_{12}GeO_{20}$ Crystal-Copper Film Interface

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Abstract

Depolarized Raman spectra have been measured in the geometry of back-scattering from the front surface of $Bi_{12}GeO_{20}$, the bulk of this crystal and the interface $Bi_{12}GeO_{20}$-copper film. The characteristics of Raman spectra for the $Bi_{12}GeO_{20}$ crystal-copper film interface have been determined and compared with those of the crystal volume. It is assumed that the oscillator parameters of the surface vibration on $Bi_{12}GeO_{20}$ crystal-copper film interface represent a result of plasmon-phonon interactions, as well as influence of defects in the frontier layer broken by mechanical polishing. The amplification coefficient of the Raman scattering on surface vibrations has been estimated.

Key words: surface enhanced Raman scattering (SERS), island copper film, cross-section of Raman scattering, phonon modes.

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Introduction

At the present time there is a continuous growth in applications of surface enhanced Raman scattering (SERS). It has been ascertained that the main reason for enhancement of Raman scattering by the molecules adsorbed on rough metal surfaces is an abrupt increase of local field intensity of light near the inflection of structured surface. Such resonances of the local field near the interface arise due to both the excitation of surface electromagnetic waves on a rough surface and local plasma resonances on the island structures. The second important origin of the SERS effect is an occurrence of coupled excited states of a molecule and a metal film. These phenomena constitute a basis of modern surface optics. The most general optical phenomena concerned with the structured surfaces have been described by electromagnetic theory [1-4].

The theory considers the SERS effect as an effect concerned with localized surface field (a near-zone field), whose structure, on the distances up to 10 nm from the surface, is related to the pattern of discrete structure of the latter. A general characteristic of the SERS effect is its observation on the molecules adsorbed on metals with high conductivity (e.g., Ag, Au and Cu). Interrelations of optical density spectra of the SERS-active substrates with the parameters of roughness of their surfaces has been established in [5]. Silver films produced by means of vacuum sputtering of silver ($p < 10^{-5}$ torr) onto the glass substrate have been used as substrates and the surface roughness has been checked using atomic-force microscope. It has been established that annealing of sputtered films leads to transformation of their surface to a quasi-periodic structure with semi-elliptical islands of about 40–80 nm in height and a smoothed nano-sized roughness. The Raman spectra of $Bi_{12}GeO_{20}$ (BGO) crystals have been earlier described in detail in [6,7]. They are characterized by high efficiency of Raman scattering. The effective cross-section of the Raman scattering measured by us amounts to

$\sigma \approx 441$, 396 and 649×10^{-28} cm^2 per one formula unit of BGO for the frequencies of 282, 330 and 548 cm^{-1}, respectively [8].

The present work is devoted to studies of characteristics of the Raman spectra obtained from the surface of $Bi_{12}GeO_{20}$ crystals overlaid with an island copper film. Our purpose is to reveal the effects of amplification and the corresponding contribution of surface phonon modes.

Samples and experimental setup

Island copper films were sputtered on a clean polished surface of BGO crystal (the plane (111)) with the aid of VUP-5M vacuum plant. The surface was subjected to ionic bombardment cleaning under the residual atmospheric pressure of 3.5×10^{-2} torr during 10 minutes. Then the cleaning in argon atmosphere at 1.5×10^{-2} torr was performed during 10 minutes. The copper film was sputtered with the thermal evaporation technique under the residual pressure of $2\cdot10^{-5}$ torr. Pieces of copper wire of 0.2–0.4 mm in diameter and overall mass of about 10 mg with 99.95% purity were used. As a result, we obtained the island copper film with the thickness of 7 nm. In order to control the film thickness, we measured its transmission and reflection at the wavelength of $\lambda = 589.3$ nm and used the Bouguer-Lambert-Beer law. Depolarized Raman spectra were measured in the back-scattering geometry for the incidence angle of 45^0 with respect to crystallographic direction [111]. The sample was excited by the second harmonic ($\lambda = 532$ nm) of acousto-optically Q-switched YAG:Nd^{3+} laser (the pulse repetition rate being 8 kHz and the average power of 100 mW). The useful signal was detected in the regime of photon counting with accumulation. The level of dark noise was N_d = 10 pulse/s. The beam was focused on the sample with high-quality lens having a short focal length (f = 1 cm). The scattered light was collected within the aperture of 7^0. We recorded the spectra resulted from focusing the incident laser beam on the front crystal surface, within the crystal volume and on the interface of the back crystal surface with the copper film. In all cases the signal-to-noise ratio for the spectral intensity was S/N = 20–90.

Results and interpretation

The resulting spectra obtained by us are presented in Fig. 1. All of the spectra reveal intense lines in the 50–600 cm^{-1} region. The main differences in those spectra lie in spectral intensity distributions and halfwidths of some spectral lines. In particular, the principal differences between the spectra from the bulk and the interface are observed in the region of 120–650 cm^{-1}. To reveal the contribution of Raman scattering from the interface we have subtracted the spectra from the bulk crystal from those obtained when focusing light on the back crystal surface covered with the copper film. Differential spectra obtained in such a way are presented in Fig. 2, together with the spectra for the bulk of BGO crystal. Table 1 shows the parameters of the phonon modes observed in the

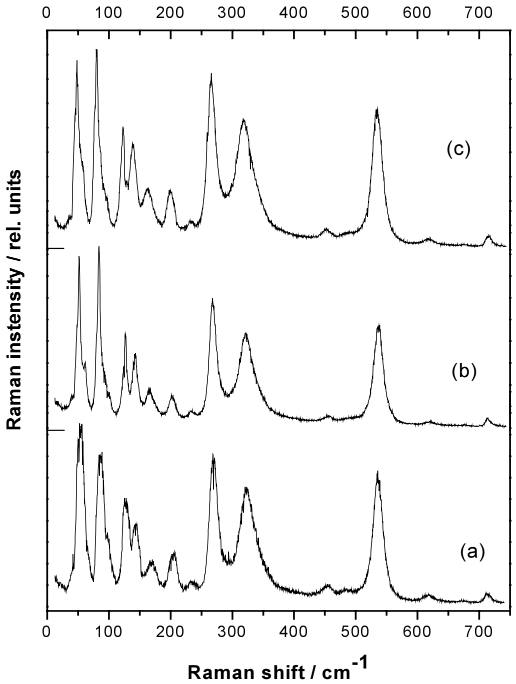

Fig. 1. Raman scattering spectra from the front surface of $Bi_{12}GeO_{20}$ crystal (a), the bulk of the crystal (b) and the interface $Bi_{12}GeO_{20}$ crystal-copper film (c).

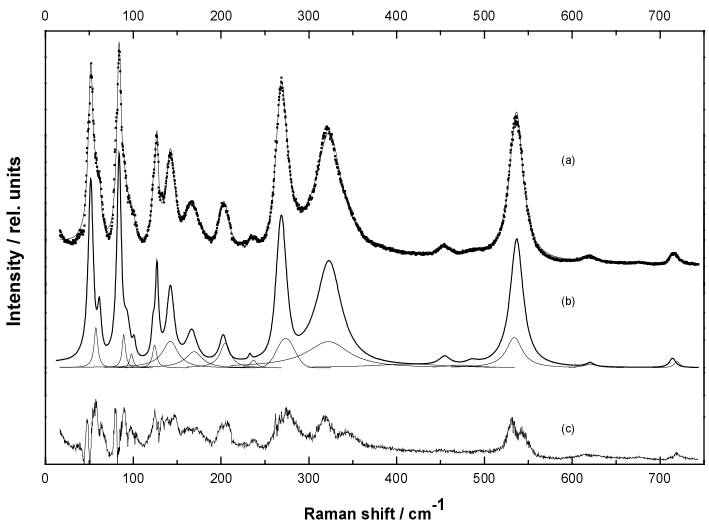

Fig. 2. Raman spectra for the $Bi_{12}GeO_{20}$ crystal-copper film interface and the corresponding fitting results (a); resulting fit of the bulk spectra for the BGO crystal (upper part) and separate Raman lines originated from the interface scattering (b); difference of the Raman spectrum for the interface and the bulk spectrum (differential spectrum) (c).

spectra, which are obtained as a result of fitting the latter on the basis of model of weakly-interacting oscillators. As seen from Table 1, the oscillator parameters of the phonon modes for differential spectrum differ from the corresponding values characteristic of the spectra obtained from the bulk crystal. The majority of the corresponding Raman lines located in the region of 120–650 cm^{-1} have lower intensity and are shifted towards the region of higher frequencies by ≤ 5 cm^{-1}, while the shifts for their halfwidths are $\leq$ 11 cm^{-1}. At the same time, there is a number of Raman lines, whose frequencies are smaller than those of the volume (57.6, 89.3, 98 and 534.3 cm^{-1}). The Raman lines with the frequencies of 420.8 and 474.1 cm^{-1} have been introduced for the best fitting of continuous intensity distributions in the region of 365–515 cm^{-1}.

It is possible to explain the observed changes in the differential Raman spectrum as a consequence of influence of plasmon-phonon interactions on the characteristics of surface vibration occurring on the $Bi_{12}GeO_{20}$ crystal-copper film interface [9], as well as the effect related to defects in the frontier layer broken by mechanical polishing [10].

Now we estimate amplification of the Raman efficiency on the example of some of the phonon modes, using the expression for the Raman scattering cross-section. The cross-section per one formula unit in the unit solid angle is determined as

$$\sigma_{Raman}(\theta,\varphi) \sim P_{Raman}\, n^2 /(d^2_{min}\, l), \qquad (1)$$

where P_{Raman} is the power of the scattered radiation, n the refractive index of crystal, d_{min} the diameter of Gaussian beam in the focal plane of the lens and l the effective length of caustic surface of the Gaussian beam in the focal plane of lens. The estimated values are d_{min} = 3.4 μm and l = 11 μm. Assuming that the differential spectrum is a result of SERS from the layer of $10a$ width (with a being the lattice constant), we can estimate the amplification coefficient:

$$K(\omega) = \frac{\sigma_{SERS}(\lambda)}{\sigma_{Raman}} = \frac{P_{SERS}}{P_{Raman}} \cdot \frac{l}{10 \cdot a}. \qquad (2)$$

The lattice constant for the $Bi_{12}GeO_{20}$ crystals is equal to $a \approx 0$ Å [11]. Then the estimated values of the amplification coefficient become as follows: K(268.6 cm^{-1})≈220, K(323.8 cm^{-1}) ≈ 440 and K(536.9 cm^{-1}) ≈ 330. These are quite reasonable values for the case of SERS

Table 1. Standard oscillator parameters of the phonon modes observed in the spectrum for the BGO crystal bulk and the same parameters for differential spectrum obtained due to fitting of the interface spectrum.

Bulk spectrum						Differential spectrum					
Frequency		Halfwidth		Intensity		Frequency		Halfwidth		Intensity	
ω	$\delta\omega$	γ	$\delta\gamma$	I	δI	ω	$\delta\omega$	γ	$\delta\gamma$	I	δI
51.8	0.1	6.7	0.1	5.3	0.1	-	-	-	-	-	-
61.6	0.1	5.0	0.3	1.0	0.1	57.6	0.1	5.2	0.4	0.9	0.1
83.9	0.1	6.0	0.1	5.3	0.1	-	-	-	-	-	-
93.2	0.2	8.3	1.0	1.2	0.1	89.3	0.1	4.5	0.4	0.6	0.1
101.0	0.2	4.2	1.0	0.3	0.1	98.0	0.3	4.9	1.1	0.3	0.1
122.4	0.2	3.8	0.6	0.4	0.1	124.4	0.2	5.7	0.8	0.6	0.1
127.0	0.1	4.7	0.2	1.9	0.1	-	-	-	-	-	-
142.5	0.1	10.4	0.3	3.4	0.1	143.1	0.5	21.6	2.2	2.5	0.3
167.0	0.2	15.0	0.7	2.1	0.1	170.1	0.8	23.0	3.1	1.6	0.2
202.6	0.2	10.6	0.6	1.3	0.1	205.1	0.3	14.5	1.1	1.5	0.1
233.0	0.6	3.6	1.7	0.1	0.0	237.1	0.8	8.2	2.7	0.3	0.1
268.6	0.1	13.8	0.1	5.1	0.1	273.6	0.3	24	0.9	1.1	0.1
323.8	0.1	34.6	0.3	15.8	0.1	325.0	1.0	59.1	5.3	6.6	0.8
-	-	-	-	-	-	420.8	20.1	100	71	1.6	1.4
454.8	0.7	15	f	0.6	0.1	-	-	-	-	-	-
-	-	-	-	-	-	474.1	7.0	44.1	36.4	0.5	0.7
486.0	2.0	15	f	0.2	0.1	-	-	-	-	-	-
536.9	0.1	17.7	0.2	9.7	0.1	534.3	0.3	22.1	1.1	2.9	0.1
620.4	1.4	10.6	4.3	0.2	0.1	621.0	2.6	20.9	9.2	0.3	0.1
714.3	0.5	8.5	1.6	0.3	0.1	719.3	0.9	8.2	3.0	0.2	0.1

occurring on the copper surface and the "green" spectral region [3].

Conclusion

In this work we have measured depolarized Raman spectra for the geometry of back-scattering from the front surface of $Bi_{12}GeO_{20}$ crystal, the bulk of this crystal and the interface between the crystal and the copper film. The main differences observed in the spectra for the bulk and the interface refer to the region of 120–650 cm^{-1}. The oscillator parameters of the phonon modes are derived with the aid of fitting of the spectra according to the model of weakly-interacting oscillators. We have revealed that the oscillator parameters of the phonon modes in case of the differential spectrum differ from the corresponding parameters characteristic of the spectra for the bulk crystal. This is explained in terms of influence of plasmon-phonon interactions on the characteristics of surface vibrations taking place on the $Bi_{12}GeO_{20}$ crystal-copper film interface, as well as the influence of defects in the frontier layer broken by mechanical polishing. Assuming that the differential spectrum is associated with SERS on the interface $Bi_{12}GeO_{20}$ crystal-copper film, we have estimated the amplification coefficient for a number of appropriate Raman lines.

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