Raman spectra of GaSe epitaxial layers grown on GaAs substrates and group-theoretical analysis of their vibrational modes

V Yu Davydov, Yu E Kitaev, A N Smirnov, I A Eliseyev, A N Starukhin, P S Avdienko, I V Sedova and S V Sorokin

Ioffe Institute, 26 Politekhnicheskaya, 194021 St. Petersburg, Russia

E-mail: valery.davydov@mail.ioffe.ru

Abstract. A complete group-theoretical analysis of vibrational modes in ε, β, γ-GaSe polytypes has been performed. Raman spectroscopy data obtained on single crystals of ε-GaSe with a subsequent group-theoretical analysis were used to analyze the Raman spectra low-dimensional GaSe structures. Information was obtained on the structural properties of epitaxial layers and arrays of nanorods of the ε-polytype GaSe grown by molecular beam epitaxy on GaAs (001) substrates.

1. Introduction

Gallium selenide (GaSe) is a layered material with a band gap depending on the thickness of the samples, highly nonlinear optical properties in the visible, infrared and terahertz spectral regions and high anisotropy of the band structure with unusual interband optical selection rules [1]. All this makes it a promising material for optoelectronic and spintronic applications. GaSe crystals are formed of vertically ordered layers ~ 0.8 nm thick, and have strong ionic-covalent bonds between atoms inside the layers and weak Van der Waals interlayer interactions. They form several polytypes (ε, β, γ, δ), differing in layer packing in a primitive cell of a bulk crystal [2]. The symmetry of a single layer (four covalently bonded Se-Ga-Ga-Se atoms) is the same in all polytypes and is described by the DG78 layer group (P6thm2). However, the symmetry of different polytypes, and hence the symmetry of normal vibrations in them, is different, which makes it possible to identify ε-, β-, γ- and δ-polytypes from the Raman spectra [3]. This paper is devoted to the experimental study of single crystals and epitaxial GaSe layers by the Raman spectroscopy method with subsequent group-theoretical analysis of vibrational modes and is aimed at developing a method for identifying the structural features and effects of polytypism in GaSe epitaxial layers grown on GaAs substrates.

2. Samples and experiment

GaSe layers were grown on GaAs (001) substrates by using a double-chamber molecular beam epitaxy (MBE) setup (SemiTEq, Russia). The standard effusion Ga cell as well as the Se valve cracking cell (Veeco, USA) with the cracking zone temperature of TSe(cr)=500°C were used as molecular beams sources. The substrate temperature (TSubstr) was varied within 400–520°C range, and layer thickness was ranged from 100 to 400 nm. According to transmission electron microscopy (TEM) data layers grown at high temperature TSubstr>500°C correspond to the ε-polytype of GaSe, there is a predominant orientation of
the c-axis along the (111) planes of the GaAs substrate. Along with epitaxial layers, we studied the ε-polytype of the GaSe single crystal, grown by Bridgman method. Raman spectra have been obtained at room temperature at the spectrometer T64000 (Horiba, France) equipped with a confocal microscope which allows one to analyze spots with 1 μm diameter. For Raman spectra excitation, the Nd:YAG laser (λex=532 nm) was used, incident light power at the sample was about 40 μW.

3. Results and discussion

3.1. Theory group analysis

When studying vibrational properties of GaSe layered crystals we start from the singular GaSe layer. It is the minimum structure unit common for all GaSe polytypes. Various polytypes differ by mutual arrangement of the same layers. As a result, the GaSe polytypes have different space groups and atomic arrangements over symmetry positions (Wyckoff positions) in the primitive unit cell. Such layer approach has been successfully applied to high-temperature superconductors [4,5] and Aurivillius compounds [6].

The symmetry of the singular GaSe layer is described by one of the 80 diperiodic groups (DG) in three dimensions (layer groups) [7], namely DG78 p6m2. There are two formula units in the layer unit cell. Two Ga atoms occupy 2e position and two Se atoms 2d positions. It should be noted that the Wyckoff positions description depends on the origin choice [8].

Using the LSITESYM program of the Bilbao Crystallographic Server [9] we determine the symmetry of phonons in the symmetry points of the 2D Brillouin zone (BZ). The mechanical representation at the Г-point of the BZ can be write down summing the contributions of the displacements of all the atoms in the primitive unit cell.

$$\Gamma_{\text{layer}} = \Gamma_{\text{ac}} + \Gamma_{\text{opt}} = 2(\Gamma_1 + \Gamma_3 + \Gamma_5 + \Gamma_6),$$

$$\Gamma_{\text{ac}} = \Gamma_3 + \Gamma_5 = A_2'' + E,'$$

$$\Gamma_{\text{opt}} = 2\Gamma_1 + \Gamma_3 + \Gamma_5 + 2\Gamma_6 = 2A_1' + A_2'' + E' + 2E''.$$

Acoustic layer modes induce interlayer bulk modes in layered crystals whereas optical layer modes transform into intralayer bulk modes.

Using the SITESYM program [9,10] we obtain bulk phonon mode symmetries in the ε-, β-, and γ-polytypes of GaSe. The results for Г-point bulk phonons are presented in table 1.

From table 1 one can see that in the primitive unit cell of γ-polytype of GaSe there is only one GaSe layer. Therefore all optical modes are intralayer ones. Since the adjacent layers belong to different primitive unit cells, the interlayer vibrations refer to the modes at the BZ boundary and hence should not be observed in the first-order Raman spectra.

In our experiments we use backscattering geometries. We obtain the Raman selection rules using the
program POLARISATION SELECTION RULES of the Bilbao Crystallographic Server [9] for the space group $P\bar{6}m2$ (SG 187). The results are given in table 2.

**Table 1.** Acoustic and optical (interlayer and intralayer) phonon modes in different GaSe polytypes.

| GaSe polytype | Symmetry | Number of layers | $\Gamma_{ac}$ | $\Gamma_{opt}$ | $\Gamma_{interlayer}$ | $\Gamma_{intralayer}$ |
|---------------|----------|------------------|---------------|----------------|------------------------|-----------------------|
| Single layer  | DG78     | 1                | $A_2^+ + E'$  | $2A_1^+ + A_2^+ + E + 2E''$ | 0                      | $2A_1^+ + A_2^+ + E + 2E''$ |
| $\gamma$      | SG160    | 1                | $A_1 + E$    | $3(A_1 + E)$   | 0                      | $3(A_1 + E)$          |
| $\epsilon$    | SG187    | 2                | $A_2^+ + E'$ | $4A_1^+ + 3A_2^+ + 3E' + 4E''$ | $A_2^+ + E'$           | $4A_1^+ + 2A_2^+ + 2E' + 4E''$ |
| $\beta$       | SG194    | 2                | $A_{2u} + E_{1u}$ | $2A_{1g} + A_{2u} + 2B_{2g} + 2B_{1u}$ | $B_{2g} + E_{2g}$ | $2A_{1g} + A_{2u} + B_{2g} + 2B_{1u} + E_{2g}$ |
|               | P6$_3$/mmc|                 |               |                |                        |                       |

**Table 2.** The Raman selection rules for the space group $P\bar{6}m2$ (Back scattering geometry).

|          | $x(yy)\bar{x}$ | $x(yz)\bar{x}$ | $x(zz)\bar{x}$ | $y(xx)\bar{y}$ | $y(xz)\bar{y}$ | $y(zz)\bar{y}$ | $z(xx)\bar{z}$ | $z(xy)\bar{z}$ | $z(yy)\bar{z}$ |
|----------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| $A_1$    | $\times$       | $-$            | $\times$       | $\times$       | $-$            | $\times$       | $\times$       | $-$            | $\times$       |
| $E'$     | $-$            | $\times$       | $-$            | $-$            | $\times$       | $-$            | $-$            | $-$            | $-$            |
| $E'(LO)$ | $\times$       | $-$            | $-$            | $-$            | $-$            | $-$            | $-$            | $-$            | $-$            |
| $E'(TO)$ | $-$            | $-$            | $\times$       | $-$            | $-$            | $\times$       | $\times$       | $\times$       | $\times$       |

**3.2. Raman data**

The studies of thin epitaxial GaSe films impose certain restrictions on Raman scattering geometries. For incident light with 532 nm wavelength corresponding to energy of 2.33 eV within the GaSe fundamental absorption range, the used scattering geometries usually are $z(xx)\bar{z}$ or $z(xy)\bar{z}$. Here $z$ is the direction being perpendicular to the layer plane whereas $x$ and $y$ directions are orthogonal and arbitrary oriented within the layer plane. The use of only two scattering geometries mentioned above significantly restricts the analytical capabilities of Raman spectroscopy for GaSe thin layer studies. However, as will be shown below, the knowledge of complete information on GaSe Raman spectra allows one to reveal fine structure details of GaSe epitaxial layers. To this end, we made our own comprehensive studies of Raman spectra of the $\epsilon$-polytype of GaSe single crystal using all possible scattering geometries given in table 2.

The polarized Raman spectra of the $\epsilon$-polytype of GaSe single crystal for various back scattering geometries are presented in figure 1. The mode frequencies are given in the last column of table 3. Based on the group theoretical analysis, we assign the predicted mode symmetries to the observed Raman spectra lines.
**Figure 1.** Polarized Raman spectra of the ε-polytype of GaSe single crystal

**Table 3.** Raman line frequencies and corresponding mode symmetries in the ε-polytype GaSe.

| Mode number | Mode type | Mode symmetry | Scattering geometry | Frequency, cm⁻¹ |
|-------------|-----------|---------------|---------------------|-----------------|
| 1           | Interlayer | E'            | z(xx, xy)z, x(yy)z  | 19.2            |
| 2           | Interlayer | E''           | x(yz)z             | 59.0            |
| 3           | Intralayer | A₁'           | z(xx)z, x(yy)z     | 134.4           |
| 4           | Intralayer | A₁''          | x(yy)z             | 144.5           |
| 5           | Intralayer | E''           | x(yz)z             | 209.3           |
| 6           | Intralayer | E(LO)         | z(xx, xy)z,       | 213.2           |
| 7           | Intralayer | E(TO)         | x(yy)z             | 232.1           |
| 8           | Intralayer | E''           | x(zz, yz)z         | 250.0           |
| 9           | Intralayer | A₁'           | x(yy)z             | 253.2           |
| 10          | Intralayer | A₁''          | z(xx)z, x(yy)z     | 307.7           |
Our analysis predicts two interlayer modes $A_2^+ + E'$ with only $E'$ mode being the Raman-active one. When assigning spectral lines we should take into account that the interlayer modes should have low frequencies. Thus, the line 19.2 cm$^{-1}$ is supposed to be the $E'$ mode. Indeed, it has been observed in $z(xx) \vec{z}$, $z(xy) \vec{z}$, and $x(yy) \vec{z}$ geometries which completely correspond to the selection rules (table 2). Next, according to our analysis (see tables 1 and 2), ten intralayer optical modes could be observed in Raman spectra, namely $4A_1$, $2E$ and $4E'$. Based on the Raman selection rules, we unambiguously identify 59.0, 134.4, 209.3 and 307.7 lines as $E'$, $A_1$, $E'$ and $A_1$, correspondingly. We also identified other modes taking into account both selection rules and the set of intralayer modes.

Raman spectroscopy data obtained on single crystals of $e$-GaSe with a subsequent group-theoretical analysis (table 3) were used to analyze the Raman spectra low-dimensional GaSe structures. It is shown that GaSe epilayers grown at $T_S=400^\circ$C belong to the $e$-polytype and the $c$-axis of the layers is directed normal to the growth surface.

In figure 2, we present as an example the polarized Raman spectra of the #0-928 sample formed by an array of GaSe nanorods, which was grown at $T_S=520^\circ$C. The pronounced difference in spectra for $z(xx) \vec{z}$ and $z(yy) \vec{z}$ scattering geometries is clearly seen. The comprehensive analysis based on the complete set of data in table 2 allows one to conclude that the grown nanorod array is a strictly oriented one. Note that the optical $c$-axis in nanorods is 45°–inclined with respect to the substrate plane and its projection is oriented along the [110] or [110] direction of the GaAs substrate. This conclusion completely agrees with the results obtained with scanning electron microscopy (SEM) on the same sample shown in figure 3.

4. Conclusion
Summing up we have performed the comprehensive group-theoretical analysis of phonon symmetry in three ($e$, $\beta$, $\gamma$) GaSe polytypes and have obtained their genesis from the phonon modes of their common structural unit, namely isolated GaSe layer. As a result we could separate interlayer and intralayer modes in all polytypes and have shown that the interlayer modes are absent in the $\gamma$-polytype. Using the combination of Raman data and group-theoretical results we have studied the structure of epitaxial films and nanorod arrays grown by MBE on GaAs (001) substrates at the substrate temperature within the $T_S = 400–520^\circ$C interval. It was shown that the GaSe epilayers grown at $T_S=400^\circ$C belong to the $e$-polytype with the $c$-axis of the layers directed normal to the growth surface. In turn, the nanorod array grown on GaAs (001) substrates at $T_S > 500^\circ$C is inclined to the...
substrate plane and its projection is oriented along the \( [1\bar{1}0] \) or \( [\bar{1}10] \) direction of the GaAs substrate. This conclusion completely agrees with the results obtained with TEM and SEM measurements on the same sample. Thus the combination of symmetry analysis with Raman experiments has been proved to be a powerful tool for identification of numerous GaSe polytypes.

References
[1] Zhou X, Cheng J, Zhou Y, Cao T, Hong H, Liao Z, Wu S, Peng H, Liu K and Yu D 2015 J. Am. Chem. Soc. 137, 7994
[2] Kuhn A, Chevy A and Chevalier R 1975 Phys. Status Solidi A 31, 469
[3] Irwin J C, Hoff R M, Clayman B P, Bromley R A 1963 Solid State Commun. 13, 1531
[4] Kitaev Yu E, Limonov M F, Mirgorodsky A P, Panfilov A G and Evarestov R A 1994 Phys. Solid State 36, 475
[5] Kitaev Yu E, Limonov M F, Panfilov A G, Evarestov R A and Mirgorodsky A P 1994 Phys. Rev. B 49, 9933
[6] Kitaev Yu E, Aroyo M and Perez-Mato J M 2007 Phys. Rev. B 75, 064110
[7] International Tables for Crystallography, Vol. E: Subperiodic groups, Eds Kopský V, Litvin D B (Kluwer, Dordrecht, 2002).
[8] Boyle L L, Lawrenson J E 1973 Acta Crystallogr. A 29, 353
[9] Aroyo M I, Perez-Mato J M, Capillas C, Kroumova E, Ivantchev S, Madariaga G, Kirov A and Wondratschek H 2006 Z. Kristallogr. 221, 15; Bilbao Crystallographic Server www.cryst.ehu.es
[10] Aroyo M I, Perez-Mato J M, Orobengoa D, Tasci E, de la Flor G and Kirov A 2011 Bulg. Chem. Commun. 43, 183