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Pressure-Dependent Phonon Scattering of Layered GaSe Prepared by Mechanical Exfoliation

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Few-layered gallium selenide (GaSe) is obtained by using the mechanical exfoliation method, and its properties are characterized by photoluminescence and Raman spectroscopy. The pressure-dependent phonon scatterings of bulk, few-layered, oxidized few-layered GaSe are characterized up to 30 GPa by using a diamond anvil cell with inert argon used as the pressure transmission medium. All the GaSe samples processed a phase transition around 28 GPa. A new vibration mode at 250 cm^{-1} is found in oxidized few-layered GaSe by Raman spectra, which is indexed as the Raman vibration mode of α-Se.

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The atomically thin two-dimensional (2D) materials, possessing unique properties, such as flexibility, transparence and a tunable bandgap, have attracted much more attention for their potential applications in electronics and photonics devices.[1−6] The layers of 2D materials are weakly coupled to each other by van der Waals force while atoms in each layer connected via covalent bonds, which makes the properties of layered materials strongly dependent on their thickness.[7] Gallium selenide (GaSe), one of the most prominent members of 2D materials, has attracted much more attention in the last few decades. Bulk GaSe crystals with hexagonal structures[8] are a direct-gap semiconductor, and show excellent optical and electrical properties arising from their peculiar layered structures.[9] Furthermore, few-layered GaSe materials provide additional advantages, which cannot be achieved in bulk forms and make them be candidates for electronics, nonlinear optics, terahertz generation, especially photo-detection applications with low dark current, high photoresponsivity, and ultra-fast response time.[10] Detailed information on the structural, optical, and electrical properties of few-layered GaSe are important to the evaluation of their potential applications in high-quality devices.

On the other hand, the high-pressure technology is a powerful tool for tuning the bandgaps of materials, investigating the structures of 2D materials such as the superconductive MoS_2, $MoSe_2$ and $ReSe_2$.[11,12] In a previous work, a hexagonal type to an NaCl-type phase transition at around 29 GPa in the bulk sample has been demonstrated, but the pressure dependence of few-layered GaSe has not been reported yet. Moreover, many problems arising from its special oxidation mechanism in ambient atmosphere limit their applications. In the past few years, researchers have only reported the physical properties of bulk GaSe, and there are rarely reports on few-layered GaSe.[13−16]

In the present work, few-layered GaSe flakes were fabricated by the mechanical exfoliation method, and the pressure-dependent phonon behaviors of bulk, few-layered, and oxidized few-layered GaSe were investigated. The high-pressure-induced phase transitions and the metallization of all the three formations are discussed in detail.

GaSe flakes were mechanically exfoliated from the bulk GaSe crystals, purchased from 2D Semiconductor Inc., onto clear and flexible poly(dimethylsiloxane) (Gel Film) substrates using adhesive tapes. Different-layered GaSe shows different colors at the same optical contrast through an optical microscope. Then, for gaining oxidized GaSe, layered GaSe was exposed to the atmosphere at room temperature for 24 hours. Afterward, layered GaSe was transferred onto a diamond anvil surface in the sample chamber via a micromanipulator. A series of high-pressure experiments were performed using a symmetric diamond anvil cell (DAC) with a pair of 300 μm culet anvils. A T301 stainless steel gasket was preindented to reduce its thickness from 250 to 50 μm and subsequently drilled in the center to form a hole of 120 μm in diameter. Measurement of the pressure of the sample chamber in DAC was achieved by collecting ruby fluorescence spectra from ruby spheres loaded in the chamber. Inert argon used as the pressure transmission medium (PTM) was compressively loaded in the sample cham-

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ber to offer a continuous hydrostatic pressure applied on the samples.

Raman and photoluminescence (PL) measurements were carried out using a micro-Raman spectrometer (Horiba-HR-Evolution) equipped with a solid-state green laser ($\lambda = 532\,\text{nm}$) in a back-scattering configuration. The PL signal was dispersed by 600 gratings/mm and the Raman signal was dispersed by 1800 gratings/mm. The laser power applied on the surface of the sample was set to be no more than 0.5 mW to avoid the probable damage from heating or oxidizing underexposure. The Gaussian spot diameter used in the fluorescence measurement system is about 1 μm.

Figure 1(a) shows the Raman spectra of GaSe crystal in the range of 100–400 cm^{-1} at room temperature. Raman modes of bulk GaSe appear at 133, 211, 251, and 306 cm^{-1}, corresponding to A^1_{1g} (out-of-plane Se–Se atoms), E^2_{2g} (in-plane Se–Se atoms), E^2_{1g} (in-plane Se–Ga atoms), and A^2_{1g} (out-of-plane Se–Ga atoms) phonon modes of bulk GaSe accordingly. The PL signal is observed in the range of 560–660 nm as shown in Fig. 1(b), and the PL band is centered at about 620 nm (2.0 eV). The PL peak has been Gaussian fitted to be A exciton 2.03 eV (610.2 nm) and B exciton 1.99 eV (620.4 nm), separately, which can be assigned as the negatively charged Trion (Coulomb-bound two electrons–one hole) and neutral exciton (Coulomb-bound one electron–one hole), respectively. The transmission process of excitons A and B can be described by Fig. 1(c). The neutral exciton B is dominant in the PL spectra. Furthermore, the difference of A and B is 0.04 eV, which can be attributed to dissociation energy. This is a common phenomenon in TMD materials.[17]

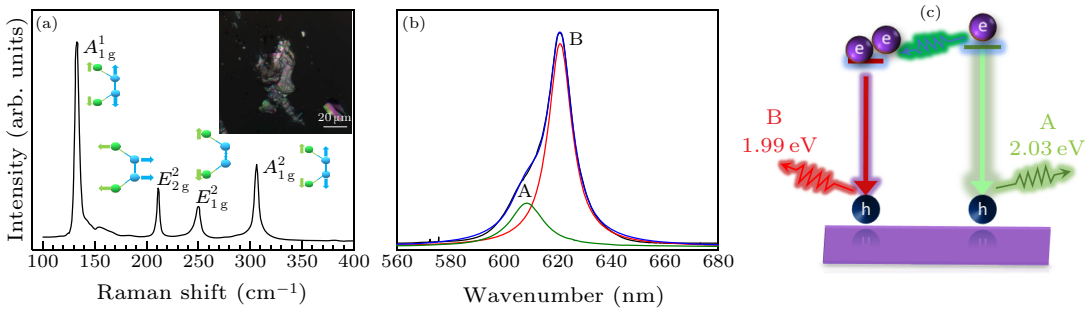

Fig. 1. (a) Raman spectrum and the corresponding vibration mode diagram of bulk GaSe. The green ball stands for Ga and the blue one is Se. (b) PL spectrum of GaSe at normal temperature and pressure, fitted with multi-Gaussian function, with individual components A and B displayed in green curves and red curves for GaSe, blue green curves for overall fitted spectra. (c) Transition diagram of excitons A and B.

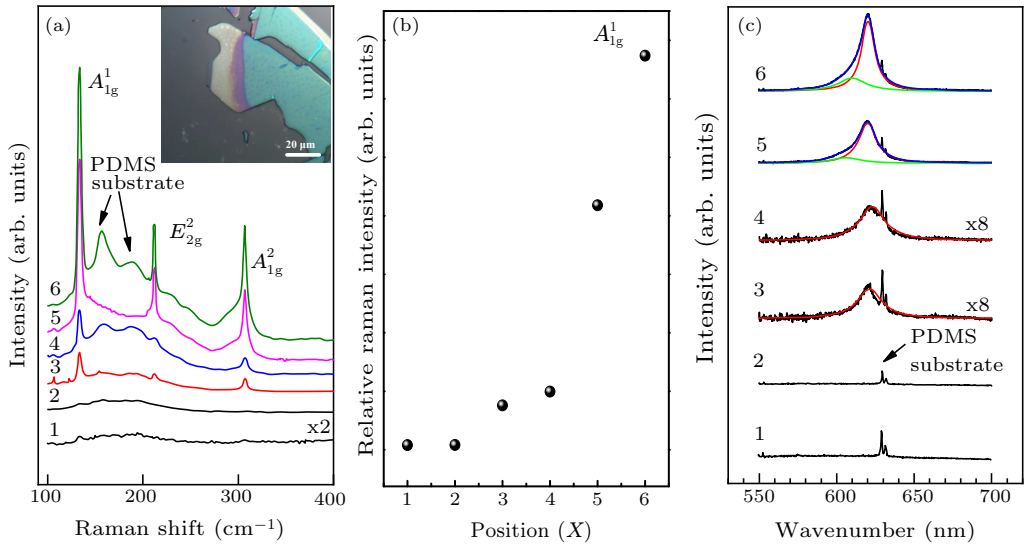

Fig. 2. (a) Comparison of Raman spectra of layered GaSe with different thicknesses, (b) the intensities of the A^1_{1g} Raman bond vs position, and (c) comparison of PL spectra for different-layered GaSe.

The few-layered GaSe flakes were obtained via the mechanical exfoliation method from the bulk GaSe crystals, as shown in the inset of Fig. 2(a). The intensities of the A^1_{1g} Raman bond vs position are shown in Fig. 2(b). As is shown, the few-layered GaSe has a smooth surface and its thickness was further characterized to six different layers of GaSe by an optical microscope due to its special optical properties. Because of the low laser damage threshold of GaSe, the common thickness measurement method will cause irre-

versible damage to it. In order to ensure the accuracy of the measurement results, there is no specific thickness measurement in our study. Herein, point 1 is the thinnest and the thickness of layered GaSe increases as the number increases. Figures 2(a) and 2(c) show the Raman and PL spectra of the corresponding points of few-layered GaSe. Compared to the bulk GaSe material, three vibration modes of A^1_{1g}, E^2_{1g} and A^2_{1g} still exist and do not show any Raman shift. This is a typical behavior observed in all GaSe films independent of the film thickness. In addition to other three vibrations, the spectra of few-layered GaSe show the disappearance of the E^2_{1g} vibration mode with peaks around 250 cm^{-1}. It is also noted that the intensity of Raman bonds becomes weaker when the thickness becomes smaller. To monitor the changes in the optical properties of few-layered GaSe, we therefore employ PL spectroscopy. Figure 2(c) shows the PL spectra of GaSe with different thicknesses at the corresponding positions, showing that the PL intensity of GaSe increases with the increase of the layer thickness. The existence of A and B excitons is observed at positions 5 and 6, and a blue shift of B excitons of around 20 meV occurs when the number of layers decreases. This phenomenon is induced by the band-gap renormalization that causes a broadening and a shift of the excitonic transition. A reduction in Raman signal strength was also observed, which is attributed to diminishing responses of spin–orbit coupling (SOC) interaction between layers. Importantly, A excitons at positions 3 and 4 would disappear when the sample thinned to a certain thickness. According to previous reports, GaSe would convert from a direct bandgap into indirect bandgap semiconductors when the layers down to 7. The process of splitting of top Γ valence band results in the change of the band structure and the quench of A excitons, and the energy band gap shows prominent reduction with the increase in the number of layers at the same time, which agree with the experimental results. We could also get a direct observation that B excitons at position 1 and 2 were quenched. Remarkably, the gap between the LCB and HVB of GaSe at the Γ point increases with the decreasing layer thickness from quantum confinement effects due to dimensionality reduction. This is the reason for the quenching of B excitons.

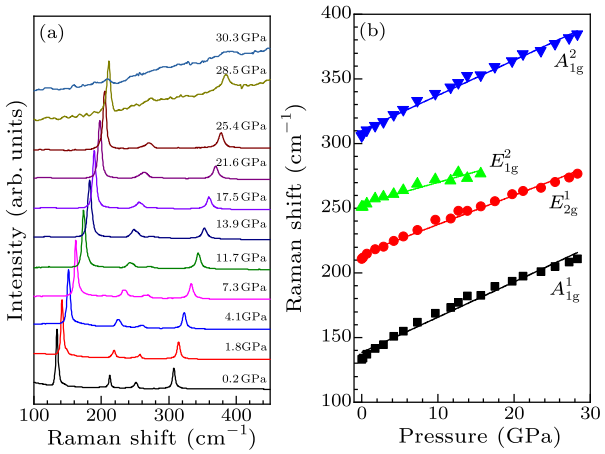

Fig. 3. (a) Raman spectra of bulk GaSe under different pressures; (b) pressure dependence of all the vibrational modes of bulk GaSe and Raman peaks as a function of pressure for bulk GaSe.

Table 1. The phase transition points and pressure derivative ($d\omega/dp$) for the Raman modes of GaSe in bulk, layered and oxidized layered forms.

GaSe	$d\omega/dp$ (cm^{-1}/GPa)			Phase transition (GPa)
	A^1_{1g} (133 cm^{-1})	E^2_{2g} (211 cm^{-1})	A^2_{1g} (306 cm^{-1})	
Bulk	2.73	2.26	2.72	30.3
Layered	3.03	2.46	2.94	27.9
Oxidized layered	2.90	2.39	2.97	28.1

We investigate the high-pressure Raman spectra of bulk GaSe up to 30 GPa as shown in Fig. 3(a). As pressure continuously increases, all modes show blueshifts up to 15.4 GPa as shown in Fig. 3(b), revealing that bulk GaSe has great compressive properties. Thus, high pressure Raman data indicates the stability of the structure at least up to the pressure ∼15.4 GPa. The Raman shift of vibration mode versus pressure can be fitted linearly as shown in Table 1. As pressure can effectively reduce the interlayer distance and strengthen the interlayer coupling and restoring force, the four peaks give all blue shift during compression, accompanied by peak broadening. In addition, we observed no discontinuity in the pressure dependence of E^2_{1g} at pressure ∼7.3 GPa, which is inconsistent with the research results of Takumi *et al.*[18] The disappearance E^2_{2g} mode in the Raman spectra at pressure ∼15.4 GPa indicates the onset of a structural phase transition. Furthermore, the Raman signal noise increases at pressure ∼28.5 GPa, which indicates that the vibration mode of the bulk GaSe is gradually softened and the crystal lattice distortion appears. Meanwhile, all the Raman vibration modes disappear, and the samples appear to be an irreversible phase transition to the NaCl structure when the pressure up to the highest pressure (30.3 GPa), as listed in Table 1. This result agrees well with the previous work.[14,15]

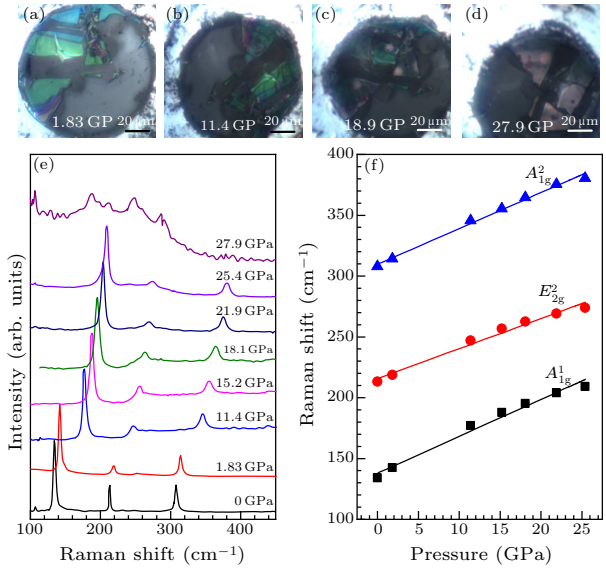

Fig. 4. Microscopy images of layered GaSe under (a) 1.83 GPa, (b) 11.4 GPa, (c) 18.9 GPa, (d) 27.9 GPa. (e) Raman spectra of layered GaSe under different pressures. (f) Pressure dependence of all the vibrational modes of layered GaSe.

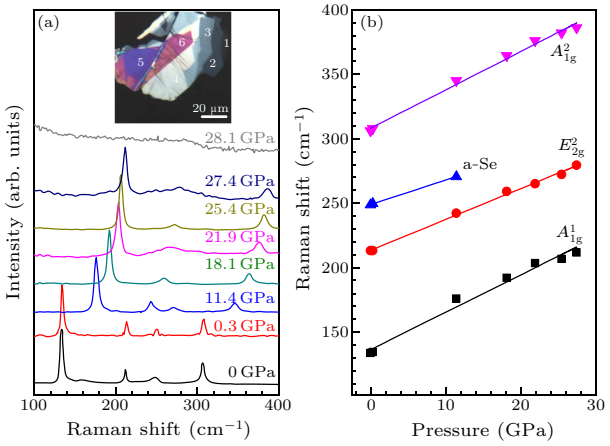

Fig. 5. (a) Raman spectra of oxidized GaSe under different pressures. The inset shows the microscopy image of oxidized GaSe flake on diamond. (b) Pressure dependence of all the vibrational modes of oxidized layered GaSe.

Figures 4(a)–4(d) show the microscopy images of layered GaSe in the DAC under different pressures. From the microscopy images we can see that layered GaSe exhibits a transparent-to-translucent process at 18.9 GPa and then opaque with metallic luster at 27.9 GPa. Figure 4(e) gives the pressure evolution of Raman spectra of the few-layered GaSe. All the vibration modes have the same pressure dependences as the bulk materials, and observable up to 25 GPa. Figure 4(f) shows the pressure dependence of the frequencies of the vibration peaks and are fitted linearly. The pressure coefficients of the frequencies of some modes are listed in Table 1, which reflects that the shift speeds are faster than the bulk one, and by contrast few-layered GaSe is more sensitive to the pressure. Moreover, the phase transition similar to the bulk one occurs in the layered GaSe. However, it is finished at 27.9 GPa, which is about 2.4 GPa lower than bulk GaSe, as listed in Table 1. This is attributed to changes of the number of GaSe layers, which reduces the SOC interaction and thus weakens the compressive strength. Furthermore, it also shows a metallization process at 27.9 GPa as shown in Fig. 4(d).

In order to investigate high-pressure Raman spectra of oxidized layered GaSe, the layered GaSe was exposed to the atmosphere at room temperature for 24 hours. The optical microscopy image results show that the surface of GaSe oxidizes with the white spot formed in atmosphere over this time frame as shown in the inset of Fig. 5(a). Three Raman modes were observed at energies of 133, 211 and 306 cm^{-1}, which can be assigned to A^1_{1g}, E^2_{2g} and A^2_{1g} modes, respectively. In addition, there is a new broad weak band at 157 cm^{-1}, which can be attributed to the Ga_2Se_3 in the oxidized layered GaSe, according to Ref. [19]. Another vibration mode at 248 cm^{-1} was observed, which can be assigned as the vibration mode from amorphous selenium (a-Se). The additional species beyond that of GaSe exists in the oxidized flake which can be traced back to formation of a-Se during the oxidized process.[19] The analysis of the path of chemical reaction can help us to reveal the nature of the new lines and the impact of water. The addition of water molecules to the photo-induced process of GaSe oxidized should lead to the formation of gallium hydroxide and hydrated selenium oxide. Consequently, the path of reaction should be expressed as[20,21]

$$2\mathrm{GaSe} + 5\mathrm{H_2O} + \frac{7}{2}\mathrm{O_2} \rightarrow 2\mathrm{Ga(OH)_3} + 2\mathrm{SeO_2 \cdot H_2O}, \quad (1)$$

$$2\mathrm{Ga(OH)_3} \rightarrow \mathrm{Ga_2O_3} + 3\mathrm{H_2O}, \quad (2)$$

$$\mathrm{H_2SeO_3} \rightarrow \mathrm{Ga_2O_3} + 3\mathrm{H_2O}, \quad (3)$$

$$\mathrm{SeO_2} \rightarrow \text{a-Se} + \mathrm{O_2}. \quad (4)$$

The high-pressure Raman spectra of oxidized layered GaSe were obtained as shown in Fig. 5(a). Like few-layered GaSe, Raman active vibration modes A^1_{1g}, E^2_{2g} and A^2_{1g} exhibit blueshift with increasing pressure, while the pressure coefficients for the frequencies of three modes change faster than the bulk one and slower than the few-layered one, as listed in Table 1. Meanwhile, the phase transition is finished at the pressure 28.1 GPa, which is earlier than the bulk one and later than the few-layered one, as listed in Table 1. Moreover, the bond attributed to the Ga_2Se_3 at 157 cm^{-1} is too weak to be detected under pressure, we do not investigate the further pressure-dependent lattice vibration properties. Noticeably, the special a-Se vibration mode at 248 cm^{-1} shows blueshift and is unobservable up to 18.1 GPa, which is consistent with the high-pressure Raman measurement behavior of a-Se substance. Table 1 gives the information

concerning about the pressure combined action of Raman bonds from different formations of GaSe. The layered GaSe has the fastest shift speed due to the weak SOC. The oxidized layered GaSe has a little slower shift speed than the layered one, which should be attributed to the oxygen replacing the selenide and then influencing the in-plane lattice of layered GaSe. Thus, the discrepancy in the pressure of phase transition may be due to different pressure sensitivities of three samples with different SOCs.

In summary, the evolution of crystal structure and exciton properties of bulk, few-layered GaSe have been studied by Raman spectroscopy and PL spectroscopy measurements. The negatively charged trion and neutral exciton bonds are observed in bulk GaSe, and the PL properties dependent on layers are also discussed. The absence of E^2_{2g} vibration mode and B exciton in few-layered GaSe can be assigned to the process of splitting of top Γ valence band within the process of thickness reduction. Meanwhile, the high-pressure Raman spectra of bulk GaSe crystals, few-layered and oxidized few-layered GaSe have been measured in the DAC with inert argon used as PTM, undergoing an irreversible pressure-induced phase transition, with metallization at 30.3, 27.9 and 28.1 GPa, respectively. Specifically, we first gain the evidence that a-Se is in the oxidized GaSe by high-pressure Raman measurement, which is due to the replacement between O and Se in the oxidation process of GaSe crystal, thus forming Ga_2O_3 and precipitation of a-Se.

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