Effect of adding Te to layered GaSe crystals to increase the van der Waals bonding force

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Effect of adding Te to layered GaSe crystals to increase the van der Waals bonding force

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The interplanar binding strength of layered $GaSe_{1-x}Te_x$ crystals was directly measured using a tensile testing machine. The $GaSe_{1-x}Te_x$ crystals were grown by a low temperature liquid phase solution method under a controlled Se vapor pressure. The stoichiometry-controlled $GaSe_{1-x}Te_x$ crystal has the ε-polytype structure of GaSe, where the Te atoms are substituted for some of the Se atoms in the GaSe crystal. The effect of adding Te on the bonding strength between the GaSe layers was determined from direct measurements of the van der Waals bonding energy. The bonding energy was increased from $0.023 \times 10^6 \, \text{N/m}^2$ for GaSe to $0.16 \times 10^6 \, \text{N/m}^2$ for $GaSe_{1-x}Te_x$ (x = 0.106). *Published by AIP Publishing.* https://doi.org/10.1063/1.4986768

I. INTRODUCTION

Two-dimensional (2D) layered materials have attracted much interest because of their unique crystallographic structure and potential applications.[1–4] Layered crystals combine thin sheets by out-of-plane van der Waals interactions. In particular, crystals formed from layers of GaSe are promising for both optical and electronic applications.[5–9] Wide-frequency-tunable terahertz (THz) waves can be generated from GaSe crystal based on the non-linear optical (NLO) process such as difference frequency generation (DFG).[5–7] GaSe crystal has a high second-order NLO coefficient ($d_{22} = 54 \, \text{pm/V}$). This means GaSe THz emitter based on DFG is expected to be a highly efficient THz source. Besides, GaSe crystal is birefringent which allows collinear phase matching for THz generation via the DFG process. The electron transport properties of GaSe are also expected to make it a useful material in the field of spintronics.[8,9] For practical applications that use 2D layered materials such as GaSe, the mechanical strength needs to be high. For example, device fabrication processes, such as dicing and wire bonding, require the crystal to be mechanically strong. However, so far, only theoretical studies have been done on the mechanical properties of 2D layered structures.[10–12] Very few experimental studies have been done.[13–15] These experimental studies have examined the van der Waals bonding energy of graphite, MoS_2, BN, PtS_2, $FePS_3$, and black phosphorus with the aid of microscopy.[13–15] In this study, direct measurements of the bonding energy were carried out on layered GaSe semiconductor with Te added to it. The addition of Te to GaSe strengthens the bonding energy between the layers. Since the strength of van der Waals bonding is closely related with the fluctuation of electron cloud distribution within an atom, the number of surrounding electrons, thus, high atomic number elements is considered to strengthen the bonding between the layers.[16] Actually, whereas only a few theoretical reports have shown the

mechanical properties of layered semiconductors using first-principles pseudopotential method within density-functional theory[12] and it has been predicted that the shear stiffness of GaSe is considerably increased when In is incorporated,[17] within our best knowledge, no direct experimental determination has been carried out for layered semiconductors. Therefore, quantitative and direct measurements of the bonding energy are required in order to obtain a crucial understanding of 2D semiconductor materials. Until now, the $GaSe_{1-x}Te_x$ crystals have been investigated for modification of GaSe optical properties[18–22] and frequency conversion efficiency.[23–27]

II. EXPERIMENTAL

Whereas most of the previous investigations of GaSe have been conducted using high temperature Bridgman melt grown crystals or vapor transport hetero epitaxial structure, present $GaSe_{1-x}Te_x$ crystals were grown by low-temperature solution growth under a controlled Se vapor pressure.[28–30] The solution growth is carried out at a temperature of $200\,^\circ\text{C}$ lower than the melting point of GaSe, and has potential, as follows: (1) Polytype growth can be suppressed. Only ε-GaSe can be selectively grown based on the phase diagram of Ga-Se.[31] (2) The concentration of point defects is reduced at thermal equilibrium. A crystal is grown from a stable supersaturated solution, and the crystal growth equipment has no mechanical moving parts. Unexpected nucleation can be escaped, and the crystallinity improved.

Three samples (undoped GaSe, GaSe with 0.6 at. % Te, and GaSe with 10.6 at. % Te) were prepared with different amounts of Te in the solution (0 at. %, 2 at. %, 20 at. %), respectively.[30] The samples were cleaved to measure the strength of the interlayer bonding using a tensile testing equipment, as shown in Fig. 1. Two stainless steel L-shaped sliders were combined, with a strain gauge between them. One slider was fixed to the GaSeTe crystal using highly adhesive double sided tape. The adhesive force between the tape and the metal was $7.5 \times 10^5 \, \text{N/m}^2$. The crystal was

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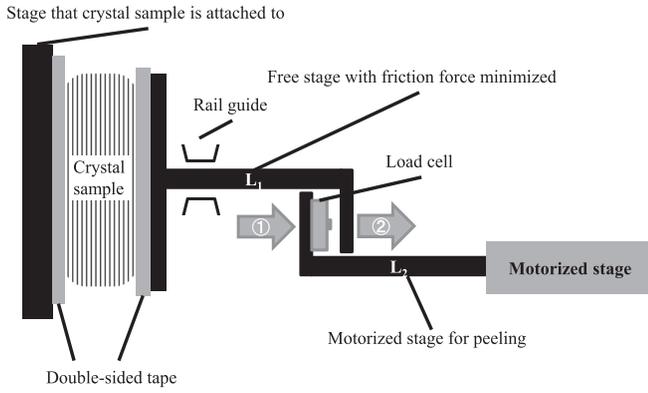
FIG. 1. Schematic of tensile testing machine used to measure the bonding energy between the layers of GaSeTe crystals.

anchored at the opposite side using the same tape. The other slider was fixed to a position-controlled stepping motor and moved with a velocity of 50 μm/s.

Te composition of grown crystals were determined by the wavelength dispersive X-ray fluorescence (WDXRF) measurements using a S8 Tiger (Bruker AXS Co., Ltd.) equipment.[30] Measurements were carried out in a helium atmosphere using LiF as a dispersion crystal. The diameter of the X-ray beam was 8 mm, which was larger than the diameters of all the grown crystals.

Room temperature photoluminescence (PL) spectra were also measured using a Nanofinder 30 (Tokyo Instruments, Inc.) to confirm the Te composition.[30] The excitation light used was 532 nm emission line from a YVO$_4$ SHG laser. The relationship between Te composition and the band to band PL peak energy was confirmed.

X-ray diffraction measurements were applied to identify the crystal structure and lattice constants of the grown crystals using a D8 ADVANCE (Bruker AXS Co., Ltd.) with CuKα radiation.[30] The identification of grown crystal phase and Te composition is very important, because it has been reported that in GaSe$_{1-x}$Te$_x$, there is a phase transition from hexagonal GaSe to monoclinic GaTe structure in the composition range $0.26 < x < 0.60$.[32] Thus, in the case of GaSe$_{1-x}$Te$_x$, we have limited our bonding force measurements to the maximum Te composition value well below x $\sim$0.26 because the comparison of bonding forces between the monoclinic and hexagonal layered crystals are not quite meaningful.

Table I shows the crystal growth conditions, Te doping conditions, and thickness for each grown crystal. Based on the WDXRF measurement results, Te composition x of grown crystals with conditions A, B, and C (Te charge: 0 at. %, 2 at. %, and 20 at. %) were found to be 0, 0.006, and 0.106, respectively. The thickness was measured by using an

TABLE I. Te compositions of liquid phase grown GaSe$_{1-x}$Te$_x$ measured by the wavelength dispersive X-ray fluorescence (WDXRF) measurements.

Mixed crystal samples	Amount of Te in Ga solvent (at. %)	Te composition X in GaSe$_{1-x}$Te$_x$	Thickness (μm)
A	0	0	270
B	2	0.006	190
C	20	0.106	380

optical microscope. Under the present growth conditions, the maximum Te composition x obtained was about 0.1, which will be due to the solubility limit reported in the literature.[33] Te composition x was also confirmed from the room temperature photoluminescence results as the red shift of band to band luminescence resulting from the addition of Te into GaSe.[30] From these results, the maximum Te composition x of grown GaSe$_{1-x}$Te$_x$ is about 0.1; therefore, it is considered that no phase transition should be occurred from hexagonal to monoclinic structure. Indeed, it was confirmed from the X-ray diffraction results that the present GaSe$_{1-x}$Te$_x$ mixed crystals grown under different conditions (B and C) have shown similar layered structure to ε-type GaSe.[30]

III. RESULTS AND DISCUSSION

The results of the bonding force measured by the strain gauge and the corresponding distance moved by the slider are shown in Fig. 2. These results confirm that all the crystal samples were elastically deformed, before reaching the maximum force, marked by solid line circles in Fig. 2, before cleaving. The parts of the curves encircled by the dotted line circles in Fig. 2 are attributed to the frictional force between the moving slider and the guide rail. We subtracted the friction force, F_{fric}, from the maximum force, F_{max}, to obtain the interlayer bonding force in the crystal. For each crystal sample, this measurement is performed several times until the friction force is constant immediately after cleavage, where the exfoliation of mutually opposed sheets occurred against the interlayer binding strength in a moment. On the other hand, the step-by-step decrease in friction force indicates that the layers are cleaved gradually. Furthermore, in order to evaluate the strength per unit area, photographs of the cleaved crystals were taken (inset in Fig. 2) and the areas of the crystals, S, were measured. The maximum stress, σ_{max}, is obtained from the following equation:

$$\sigma_{max} = \frac{F_{max} - F_{fric}}{S}. \tag{1}$$

We consider this to be the bonding energy of the crystal. The results for the different crystal samples are shown in Fig. 3.

We compare the interlayer bonding strength of crystals with different Te composition. Consequently, compared to liquid phase grown GaSe, the crystals with Te added were strengthened and the bonding energy increased with the higher amount of Te, indicating that the addition of Te is effective for increasing the interlayer bonding in GaSe crystals. Plane orientation of the crystals has been confirmed along c-axis by the XRD measurements.[30] However, it is considered that for layered crystals, when the crystals have defects such as vacancy, interstitial atom, dislocation, grain boundary and stacking fault, the interlayer binding energy will not be strengthened.

van der Waals bonding is constructed with some kinds of bonding forces, i.e., permanent dipole force, induced dipole force, and dispersion force. From these three bonding forces, the total van der Waals bonding force E is expressed as follows:[34]
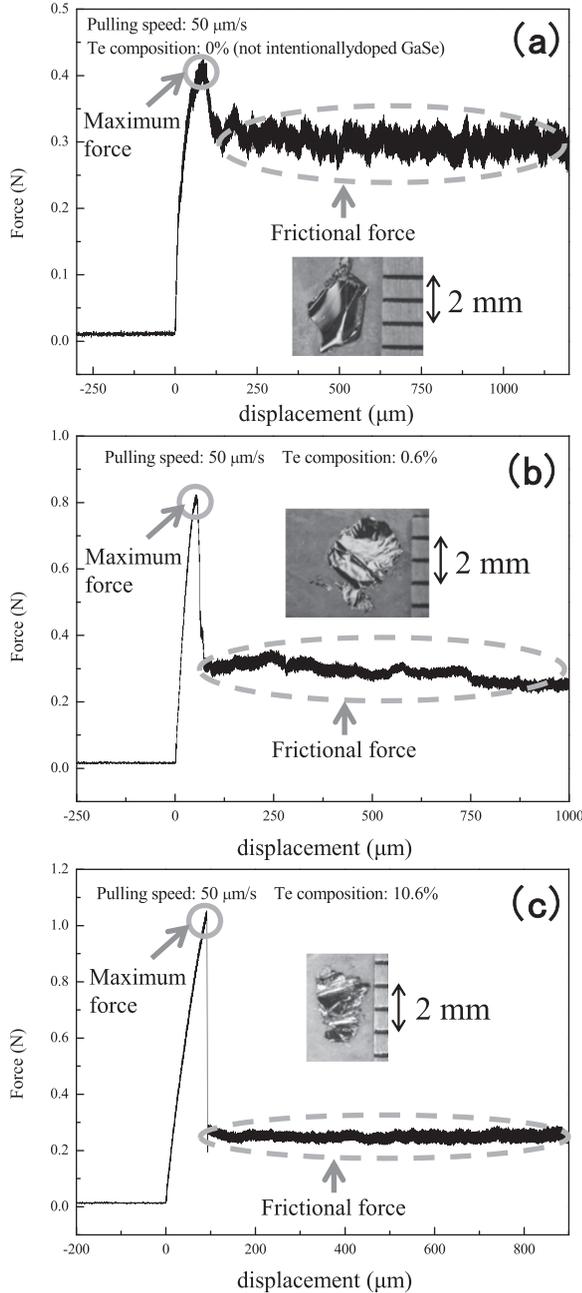
FIG. 2. Force measured by the strain gauge against the position of the slider, x ($x = 0$ denotes the contact position) for GaSe (a) and GaSe$_{1-x}$Te$_x$ crystals with Te compositions of 0.006 (b) and 0.106 (c). Inset: photographs of the surfaces of the cleaved crystals.

$$E = -\frac{1}{r^6}\left\{\frac{2\mu_1^2\mu_2^2}{3kT} + \mu_1^2\alpha_2 + \mu_2^2\alpha_1 + \frac{3}{4}\frac{h\alpha_1\alpha_2\nu_1\nu_2}{(\nu_1+\nu_2)}\right\}, \quad (2)$$

where r is the intermolecular distance, k is the Boltzmann constant, T is the temperature, μ_1 and μ_2 are the dipole moments, h is the Planck constant, α_1 and α_2 are the polarizabilities, and ν_1 and ν_2 are the vibration frequencies without interatomic interaction. Thus, it is shown that the van der Waals force is a very short distance interaction with r^{-6}. Then, when constituent atoms and molecules have no permanent dipole moment completely, like an inert gas elements, μ_1 and μ_2 are zero; thus, van der Waals force is reduced to be as follows:
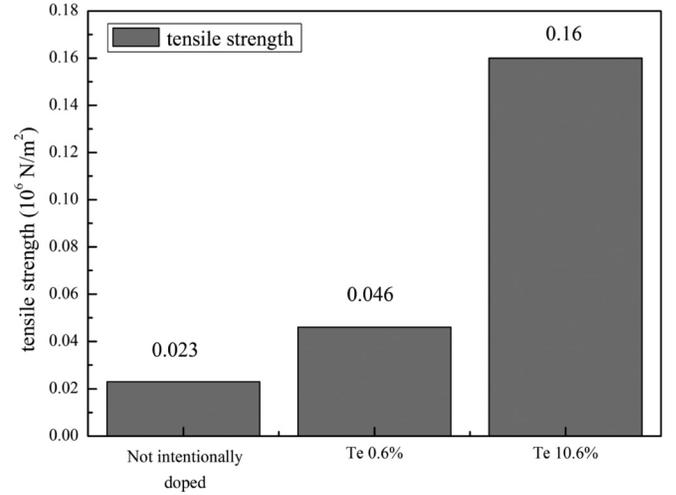
FIG. 3. Normalized bonding strengths of GaSe (a) and GaSe$_{1-x}$Te$_x$ crystals with Te compositions of 0.006 (b) and 0.106 (c).

$$E = -\frac{1}{r^6}\left\{\frac{3}{4}\frac{h\alpha_1\alpha_2\nu_1\nu_2}{(\nu_1+\nu_2)}\right\}. \quad (3)$$

As a result, it is shown that the van der Waals force is proportional to the polarizability (α_1 and α_2) of the constituent element. Electric polarizability is the relative tendency of a charge distribution of the electron cloud of an atom or molecule. Thus, it is considered that as the number of electrons of an atom is increased, electric polarizability is also increased. Actually, the electric polarizability is almost proportional to the molecular weight which is also proportional of the number of electrons.[35] Here, it is shown from the literature that the electric polarizabilities of Se and Te are 26.24 and 37.00 in arbitrary unit, respectively. Thus, the ratio of electric polarizabilities of Se and Te is about 1.4, then the ratio of van der Waals force will be about 2 between Se and Te, because the van der Waals bonding force is proportional to the products of polarizabilities. In addition, van der Waals bonding force is also proportional to the vibration frequency of atoms without interaction ν_1 and ν_2. Vibration frequency will be proportional to the atomic mass; thus, the ratio of vibration frequency between Se and Te will be about 1.6. As a result, the ratio of van der Waals bonding force between Se and Te is expected to be about 4 in the case of Te. However, this is the case when all Se is completely exchanged with Te. In our mixed crystals, Se is partially exchanged with Te, and the Te composition is determined to be about 0.1. Thus, the expected enhancement of van der Waals force due to partial exchange of Te will be 0.4 times larger than that of Se at minimum. This is about one order in magnitude smaller than that of experimentally measured results.

However, the bonding force of GaSe$_{1-x}$Te$_x$ layered structure is not from completely van der Waals bonding only like an inert gas elements; thus, the covalent bonding and ionic bonding contribution will attribute to the under estimation of the effect of the heavy element Te. But, it is shown that the soft and cleavable GaSe crystal becomes quite rigid via the enhancement of van der Waals bonding force when heavy element Te is incorporated within the framework of hexagonal crystallographic layered structure.

IV. CONCLUSION

A tensile testing machine was constructed to quantitatively determine the interlayer van der Waals bonding force in layered GaSe crystals. The bonding strength of GaSe and $GaSe_{1-x}Te_x$ crystals with different Te compositions ($x = 0.006$, 0.106) were measured experimentally. The results have shown that the interlayer bonding of $GaSe_{1-x}Te_x$ crystals was greater than that of GaSe crystals. The interlayer bonding strength of $GaSe_{1-x}Te_x$ ($x = 0.106$) was about 7 times larger than that of GaSe.

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