Temperature-Dependent Absorption of Ternary HfS$_{2-x}$Se$_x$ 2D Layered Semiconductors

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Abstract: In this study, we present the investigation of optical properties on a series of HfS$_{2-x}$Se$_x$ crystals with different Se compositions $x$ changing from 0 to 2. We used the chemical-vapor transport method to grow these layered ternary compound semiconductors in bulk form. Their lattice constants and crystal properties were characterized by X-ray diffraction, high-resolution transmission electron microscopy, and Raman spectroscopy. We have performed absorption spectroscopies to determine their optical band-gap energies, which started from 2.012 eV with $x = 0$, and gradually shifts to 1.219 eV for $x = 2$. Furthermore, we measured the absorption spectroscopies at different temperatures in the range of 20–300 K to identify the temperature dependence of band-gap energies. The band-gap energies of HfS$_{2-x}$Se$_x$ were determined from the linear extrapolation method. We have noticed that the band-gap energy may be continuously tuned to the required energy by manipulating the ratio of S and Se. The parameters that describe the temperature influence on the band-gap energy are evaluated and discussed.

Keywords: 2D semiconductors; absorption; van der Waals

1. Introduction

There is a great need for high-speed electronics with low power consumption beyond the silicon-based devices. New flexible materials for electronics and optoelectronics applications with an atomic scale thickness have resulted in much exploration [1–3]. Novel two dimensional (2D) materials have attracted significant interest because of their unique fundamental properties [4,5]. Layered 2D transition metal dichalcogenides (TMDs) materials with the chemical formula MX$_2$ (here M represents the transition metal and X represents a chalcogen) are considered to be candidates for next-generation electronic circuit applications. 2D TMD is stacked layer by layer in the form of X-M-X, consisting of two hexagonal planes of chalcogen elements [6]. The chalcogen layer-by-layer structure by van der Waals (vdW) interacts to form the bulk material, which allows for atomic control of its ultrathin thickness [7,8]. Unlike graphene without a band gap, the 2D TMDs with semiconductor behaviors can be adopted to the integration of electronic devices [9]. Up to now, 2D MX$_2$ (M = Mo or W and X = S or Se) of single- or multi-layered TMDs with ultrathin thickness have been research topics of the fields of material science and nanotechnology [10]. Due to their specific optical and physical properties, the investigations of various device structures have included the heterostructure p-n junction diode [11], field effect transistor [12,13], fin-shaped field effect transistor [14,15], phototransistor [16], energy storage and conversion [17,18], sensors [19,20], biomedicine [21–23], and water remediation [24,25].
Among these TMDs materials, only a few studies on HfX$_2$ ($X =$ S or Se) compounds have been achieved [26]. The HfX$_2$-based TMDs have high work function [27] and high mobility [28], allowing for their potential applications in nanoelectronic and optoelectronic devices [29–32]. The thermoelectric performance of HfS$_2$ is also investigated [33]. The heterostructure of graphene/HfS$_2$ as an electrode material for alkali-ion batteries is also performed [34]. However, the band gap of HfS$_2$ and HfSe$_2$ is fixed with no flexibility, which limits its ability in applications in devices. The bad gap of mixed ternary alloys can be tuned by adjusting the composition ratio, which allows for a wider detecting range in optoelectronic device applications. Due to the wide range of possible applications, the detailed temperature dependence of band-gap transitions is still unclear. Hence, more studies on the HfS$_{2-x}$Se$_x$ alloys concentrated on the temperature dependence of band-gap transitions are essential to pave the way for next-generation device applications.

In this study, the investigation of the structural properties of HfS$_{2-x}$Se$_x$ alloys measured by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), and Raman spectroscopy has been presented. We also characterized their compositions by electron probe X-ray micro-analyzer (EPMA). The band-gap energy determination of HfS$_{2-x}$Se$_x$ mixed crystals was carried out by the absorption spectroscopy. The parameters corresponding to the temperature dependence of the band-gap energies were also evaluated and discussed.

2. Experimental

Layered HfS$_{2-x}$Se$_x$ single crystals in bulk form were grown using the chemical-vapor transport method. I$_2$ (~3.63 mg/cm$^3$) was used as a transport agent for chemical transportation. A quartz ampoule with the size of 30 mm OD $\times$ 25 mm ID $\times$ 28 cm was used to contain the high-purity (Hf: 99.99%, S: 99.99%, and Se: 99.99%) constituent elements, which were weighted to fit the atomic ratio HfS$_{2-x}$Se$_x$ ($0 \leq x \leq 2$). A high-vacuum diffusion pump was used to maintained the quartz ampoule pressure at approximately 2 $\times$ 10$^{-5}$ torr during the sealing process. Then, it was put into a two-zone furnace and two automatic temperature controllers were used to control the heater to hold the high temperature zone at 800 °C, and the low temperature zone at 650 °C in a duration of 14 days. The crystals thus grown have a surface area up to 10–20 mm$^2$ and are 20–100 µm thick. In this work, the nominal composition x of six HfS$_{2-x}$Se$_x$ crystals varied as 0, 0.4, 0.8, 1.2, 1.6, and 2. The lattice structure and alloy compositions for all the HfS$_{2-x}$Se$_x$ crystals were checked by XRD and EPMA, respectively. The measured composition of the HfS$_{2-x}$Se$_x$ alloys by EPMA is listed in Table 1. The Raman spectroscopy has been performed on 3D Nanometer Scale Raman spectrometer (Tokyo Instruments, Nanofinder 30) with 488 nm laser. The laser power was set at about 1 mW to avoid the heating damages. The HRTEM images and selected area electron diffraction (SAED) patterns were taken by PHILIPS CM-200 TWIN FE-TEM to characterize the lattice structure of HfS$_{2-x}$Se$_x$ crystals.

Table 1. The measured composition (%) of the HfS$_{2-x}$Se$_x$ alloys assessed by EPMA.

| HfS$_{2-x}$Se$_x$ | Hf | S | Se |
|------------------|----|---|----|
| HfS$_2$          | 34.25 | 65.74 |
| HfS$_{1.6}$Se$_{0.4}$ | 34.32 | 53.73 | 10.93 |
| HfS$_{1.2}$Se$_{0.8}$ | 37.50 | 42.44 | 20.04 |
| HfS$_{0.8}$Se$_{1.2}$ | 34.32 | 28.39 | 37.28 |
| HfS$_{0.4}$Se$_{1.6}$ | 34.83 | 16.75 | 48.41 |
| HfSe$_2$         | 35.87 | 64.12 |

The optical properties of the HfS$_{2-x}$Se$_x$ layered single crystals were studied by absorption measurements in the temperature range of 20–300 K. The light source with a 150 W quartz-halogen lamp was adopted to a PTI 0.25 m grating monochromator, focused on the sample with near-normal light incidence and collected by a silicon photodetector. The temperature-dependent measurements were carried out by a closed-cycle cryogenic
refrigerator equipped with a digital thermometer controller with temperature stability in 0.5 K.

3. Results and Discussion

The XRD patterns of HfS$_{2-x}$Se$_x$ layered single crystals with various Se content are depicted in Figure 1a. The major diffraction peaks of HfS$_{2-x}$Se$_x$ crystals fit in the figure of the CdI$_2$ type hexagonal unit cell with the Pbnm space group. The strongest diffraction peak is assigned to the (001) plane; other diffraction peaks are assigned to the (002), (003), (004), and (005) planes [35]. The main peak position of the HfS$_{2-x}$Se$_x$ layered single crystals shifts to a lower angle gradually with increasing Se. The lattice constant c of HfS$_{2-x}$Se$_x$ crystals can be deduced according to Bragg’s law [36]. All of the XRD peaks, which are indicated as (001) to (005) from left to right, are derived from different planes stacking perpendicularly to the c-axis. Because all the XRD peaks indicate the same orientation, this result confirms the single crystalline nature of our HfS$_{2-x}$Se$_x$ crystal. In Equation (1) with the first-order approximation $n = 1$, and for the (001) orientation XRD peak located at $2\theta \approx 15^\circ$ for the HfS$_2$, we can find that $d_{001} = 0.5862$ nm. The lattice constant c can be deduced by substituting $(hkl) = (001)$ into the Equation (2); we can see that the c value is equal to the value of $d_{001}$, which is 0.5862 nm for HfS$_2$ and gradually increases to 0.6146 nm for HfSe$_2$.

$$\frac{1}{d_{hkl}^2} = \frac{2n \sin \theta}{\lambda}$$

(1)

$$\frac{1}{d_{hkl}^2} = \frac{4}{3} \left( \frac{h^2 + 2hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

(2)

Figure 1. (a) XRD patterns of HfS$_{2-x}$Se$_x$ layered crystals with varying Se compositions. (b) Lattice constant c values deduced from XRD diffraction. (c) HRTEM image and SAED pattern of HfS$_{1.6}$Se$_{0.4}$ crystal. (d) The deduced lattice constants a of HfS$_{2-x}$Se$_x$ crystals from HRTEM.

Figure 1b indicates the lattice constant c values deduced from XRD diffraction. The c value is 0.5862 nm for HfS$_2$ and gradually increases to 0.6146 nm for HfSe$_2$. The HfS$_{2-x}$Se$_x$ crystal structure was also characterized by HRTEM. Figure 1c shows the HRTEM image of HfS$_{1.6}$Se$_{0.4}$ crystal. The deduced lattice constants a of HfS$_{2-x}$Se$_x$ crystals from HRTEM
are plotted in Figure 1d. The above results indicate that the crystal stoichiometry is in agreement with the nominal value.

Figure 2a shows the characterization results of HfS$_{2-x}$Se$_{x}$ layered single crystals probed by Raman spectroscopy. The composition-dependent vibration modes of HfS$_{2-x}$Se$_{x}$ layered single crystals were assigned as A$_{1g}$ (Hf-Se), E$_{g}$ (Hf-S), and A$_{1g}$ (Hf-S). The intensity of Hf-S related Raman modes decreases with increasing Se composition, and the vibration modes of Hf-Se are enhanced gradually. In Figure 2b, the Raman vibration modes of the HfS$_{2-x}$Se$_{x}$ layered single crystals are statistically depicted. The Raman frequencies and intensity evolution with the S/Se atomic ratio are consistent with the reported literature [37] (HfS$_{2-x}$Se$_{x}$ alloys). The XRD measurements and Raman spectroscopy provide characterizations for the identification of the crystal structure and material phases of the HfS$_{2-x}$Se$_{x}$ layered single crystals.

The room temperature absorption spectra of HfS$_{2-x}$Se$_{x}$ layered single crystals with various Se contents of x = 0, 0.4, 0.8, 1.2, 1.6, and 2, respectively, are shown in Figure 3a. We can observe that the absorption edge gradually shifts to a lower energy side with increasing Se content. The atomic number of Se is larger than S, which causes the band gap decrease with increasing Se content in HfS$_{2-x}$Se$_{x}$ layered single crystals. The band-gap energies (E$_{g}$) for HfS$_{2-x}$Se$_{x}$ layered single crystals with different Se content were determined from the extrapolation of the absorption coefficient to the base line. The obtained band-gap energy values of HfS$_{2-x}$Se$_{x}$ layered single crystals at 300 K are 2.012, 1.729, 1.664, 1.543, 1.349, and 1.219 eV for Se content of x = 0, 0.4, 0.8, 1.2, 1.6, and 2, respectively. Compared to the band gap determined by the theoretical study of the HfS$_{2-x}$Se$_{x}$ monolayer, the results in study are in reasonable agreement with the reported theoretical results [38]. The discrepancy might be due to the material thickness effects and the difference between the experimental and the theoretical model. The composition dependence of the band-gap energy describes the degree of nonlinearity that can be fitted by the expression $E_{g}(x) = (x/2)E_{g}(HfSe_{2}) + (1 − (x/2))E_{g}(HfS) − bx/2(1 − (x/2))$ [36], where $E_{g}$ is the band-gap energy and $b$ is the bowing parameter. In Figure 3b, the solid line represents the fit of experimental data with above equation. In this work, $b$ is determined to be 0.54 eV, which is comparable with previous results of 0.68 eV for SnSSe [39] and 0.456 eV for ZnSSe [40] alloys. The deduced bowing parameters in this work are smaller than that the values 0.74–1.84 eV for the III-nitrides semiconductors. This might be due to the fact that the bowing parameter is dominated by various physical effects, structural and chemical disorder, atomic mismatch, strain, and carrier concentration [41].
Figure 3. (a) The experimental absorption spectra of HfS$_{2-x}$Se$_x$ layered crystals at 300 K. (b) Composition-dependent band-gap energies for HfS$_{2-x}$Se$_x$ layered crystals at 300 K.

Displayed by dotted curves in Figure 4 are the experimental absorption spectra of the HfS$_2$ layered single crystals at several temperatures between 20 and 300 K. There are a number of methods for bandgap calculation using absorption data, such as Tauc’s method, by taking $\alpha^{1/2}$ (indirect bandgap) or $\alpha^2$ (direct bandgap) methods. The relation derived by Tauc et al. [42] was intended for use with amorphous materials. They assume that the amorphous materials contain a localization of energy states; thus, absorption transitions do not need to conserve momentum. For single crystals with indirect energy gaps, the electron transition from the valence band to the conduction band, which is also understood as absorption transition, can be described by Fermi’s golden rule. The density states on both the valence and conduction bands will be included with phonon interactions to follow the rule of momentum conservation. The square root of the absorption coefficient plot could be available to extract the indirect band-gap energy [43]. As a general characteristic of most semiconductors, when the measurement temperature gradually rises, the band-gap energy exhibits a red-shift. The temperature variation of the band-gap energies obtained from the absorption measurements for the HfS$_{2-x}$Se$_x$ ternary-layered single crystals are plotted in Figure 5. The temperature-dependent evolution of the band-gap energy of the HfS$_{2-x}$Se$_x$ ternary-layered single crystals can be described by the Varshni semi-empirical model [44]:

$$E_g(T) = E_g(0) - \alpha T^2 / (\beta + T)$$

(3)

where $E_g(0)$ is the band-gap energies at 0 K. The constant $\alpha$ is related to the electron (exciton)–average phonon interaction strength, and $\beta$ is closely related to the Debye temperature. The solid curves are least-squares fits to the Varshni semi-empirical model. Obtained from the fitting procedure, the Varshni parameters for the investigated crystals and, for comparison, other layered crystals such as MoSSe, WSSe 2D-layered semiconductors [45], III–V group semiconductors such as GaAs [46] and InP [47], II–VI group semiconductors such as ZnSe [48], and IV group semiconductors such as Si [46] are listed in Table 2.

The temperature dependence of band-gap energies can also be described by an expression containing the Bose–Einstein occupation factor for phonons [49,50]:

$$E_g(T) = E_g(0) - 2a_B / [\exp(\Theta_B / T) - 1]$$

(4)

where $E_g(0)$ is the band-gap energy at 0 K, $a_B$ represents the strength of the electron (exciton)–average phonon interaction, and $\Theta_B$ corresponds to the average phonon temperature. In solid crystals, phonons play an important role in many physical properties. The variation of band-gap energy with temperature is majorly affected by lattice dilation and the electron–phonon interaction, which can be correlated with the phonon interaction [51,52].
Table 2. Materials Feature $E(0)$ $\alpha$ $\beta$ $\alpha_B$ $\Theta_B$ $dE/dT$

| Materials Feature | $E(0)$ (eV) | $\alpha$ (m eV/K) | $\beta$ (K) | $\alpha_B$ (m eV) | $\Theta_B$ (K) | $dE/dT$ (m eV/K) |
|------------------|-------------|------------------|----------|-----------------|-------------|-----------------|
| HfS$_2$          | 2.141       | 1.18            | 496      | 135             | 342         | −0.75           |
| HfS$_{1.6}$Se$_{0.4}$ | 1.849 | 0.98            | 425      | 96              | 288         | −0.66           |
| HfS$_{1.2}$Se$_{0.8}$ | 1.775 | 0.84            | 367      | 75              | 258         | −0.50           |
| HfS$_{0.8}$Se$_{1.2}$ | 1.646 | 0.69            | 300      | 67              | 250         | −0.49           |
| HfS$_{0.4}$Se$_{1.6}$ | 1.436 | 0.54            | 247      | 45              | 214         | −0.43           |
| HfS$_2$          | 1.284       | 0.35            | 169      | 23              | 161         | −0.32           |
| MoSSe            | 1.74        | 0.395           | 216      |                 |             |                 |
| WSSe             | 1.87        | 0.59            | 260      |                 |             |                 |
| GaAs             | 1.517       | 0.55            | 225      | 57              | 240         |                 |
| InP              | 1.424       | 1.02            | 823      | 35.9            | 204         |                 |
| ZnSe             | 2.800       | 0.73            | 295      | 73              | 260         |                 |
| Si               | 1.170       | 4.73            | 636      |                 |             |                 |

Ref. [45]; c Ref. [46]; d Ref. [47]; e Ref. [48]; and f Ref. [46].
The results obtained from fitting the parameter values according to the Bose–Einstein expression are listed in Table 2 as well.

The electron–phonon interaction strength parameter $\alpha$ from Varshni model can be easily related to electron–phonon interaction constant $a_B$ and average phonon temperature $\Theta_B$ from Bose–Einstein expression by taking the high-temperature limit of both expressions. This yields $\alpha = 2a_B/\Theta_B$. Obtained from the fitting procedure to the experimental data with both expressions, the parameters presented in Table 2 show that this relation is matched. From Equation (4), it is straightforward to show that the high temperature limit of the slope of $E(T)$ vs. the $T$ curve approaches a value of $-2a_B/\Theta_B$. The calculated value of $-2a_B/\Theta_B$ for band-gap transition energies equals 0.78, $-0.66$, $-0.58$, $-0.53$, $-0.42$, and $-0.28$ meV/K for Se contents ($x$) = 0, 0.4, 0.8, 1.2, 1.6, and 2, respectively, which agrees well with the value of $[dE/dT] = 0.75$, $-0.66$, $-0.50$, $-0.49$, $-0.43$, and $-0.32$ meV/K as obtained from the linear extrapolation of the high-temperature (140–300 K) absorption experimental data. It is noticed here that the temperature-dependence parameters indicate enhanced electron–phonon coupling with increasing sulfur composition. This may be due to the fact that the mass of S is lighter than that of Se Figure S1.

4. Conclusions

In conclusion, a series of HfS$_{2-x}$Se$_x$ ternary-layered single crystals were successfully grown by the chemical vapor transport method. The crystal phase properties of HfS$_{2-x}$Se$_x$ ternary-layered single crystals were characterized by XRD spectra and Raman spectra. The temperature dependence of the band-gap energy of HfS$_{2-x}$Se$_x$ ternary-layered single crystals was investigated by absorption spectroscopy in the temperature range between 20 and 300 K. Experimental data were fitted with the semi-empirical Varshni and Bose–Einstein expression. An enhanced electron–phonon coupling with higher sulfur content was observed by analyzing the parameters that describe the temperature dependence of the band-gap energies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ma15186304/s1, Figure S1: Temperature–dependent absorption spectra of HfS$_{2-x}$Se$_x$.

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