Substitutional Sulfur in CdSe: Localized Vibrational Modes

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The substitutional sulfur at the selen site in wurtzite CdSe is identified by a combination of infrared absorption spectroscopy and first principles calculations. The dominant $^{34}\text{S}$ isotope gives rise to two local vibrational modes at 270.6 and 271.4 cm$^{-1}$ (10 K) assigned to the nondegenerate $A_1$ and the twofold degenerate $E$ representations of the $C_{3v}$ point group. The corresponding signals of the $^{34}\text{S}$ isotope occur at 263.6 and 264.4 cm$^{-1}$. The results of measurements performed on a set of samples supplied by different manufacturers highlight that sulfur is an ubiquitous impurity in CdSe unintentionally incorporated into the crystals during the process of growth.

1. Introduction

Cadmium selenide (CdSe) is a direct band gap II–VI semiconductor with exceptional optoelectronic properties suitable for a wide range of applications, such as photodetectors, solar cells, light-emitting diodes, and catalysis. CdSe nanoparticles have been used in laser diodes,[1] nanotransistors,[2] for carrier multiplication in solar cells,[3] in nanosensing,[4] or biomedical imaging.[5]

Many key parameters which determine the functionality of semiconductor devices, such as minority carrier lifetime or electrical conductivity, are decisively affected by impurities and defects. Therefore, the understanding of their properties is necessary to manufacture devices with highest efficiencies.

Impurities with masses less than those of the semiconductor host atoms often give rise to infrared active local vibrational modes (LVMs), i.e., vibrations decoupled from the phonon spectrum of the crystal.[6] Such LVMs have provided important insights into the properties of substitutional impurities in binary II–VI compounds. In particular, the chemical identity of the species can be directly unveiled via the isotope mass dependence of the LVM frequencies. LVMs of substitutional Be, Mg, Ca, and S in zinc-blende CdTe and ZnTe as well as Be and Mg in wurtzite CdSe were already reported.[9–11]

First studies of sulfur in CdSe were conducted by Verleur and Barker[12] and Beserman and Balkanski,[13] who carried out infrared reflectivity measurements on mixed CdSe$_{1-x}$S$_x$ crystals. Both groups attributed signals at about 270 cm$^{-1}$ to sulfur-related vibrational modes. Further evidences for this assignment were provided by an infrared (IR) absorption study of Burger et al.[14] At present, there is a general agreement that sulfur is a common impurity in CdSe single crystals.[12,15,16] Despite this body of evidence, the exact spectroscopic features of substitutional sulfur remain unknown. The ambiguity arises from: 1) the position of the 270 cm$^{-1}$ mode in the spectrum occurring in the strong multiphonon absorption bands of the CdSe host,[17] and 2) the high concentration of sulfur in CdSe or CdSe$_{1-x}$S$_x$ samples used so far, which affects both the frequency and the line width of the corresponding spectroscopic signals. As a result, both exact vibrational modes of sulfur and more importantly its position in the crystal remain vague.

Here, we apply polarization and temperature-sensitive Fourier-transform infrared (FTIR) absorption spectroscopy to study nominally undoped as well as $^{34}$S-implanted CdSe crystals. Direct evidences are provided that the defect with a vibrational mode frequency of about 270 cm$^{-1}$ represents substitutional sulfur at the selen site (S$_{\text{Se}}$). Its microscopic nature is corroborated by first principle calculations.

2. Experimental Section

The samples used in this study were $\approx 5 \times 5 \text{ mm}^2$ single crystals with a thickness of 0.5 or 1 mm purchased from SurfaceNet GmbH, Crystec GmbH, Cradley Crystals, ANAU Berlin-lab GmbH, and the Research Institute of Material Science and Technology, Russia. Unless noted otherwise, the surface orientation of the samples was (1120).

Room-temperature implantations with $^{34}$S ions were performed at the Ion Beam Center at the Institute of Ion Beam Physics and Materials Research (Helmholtz Zentrum Dresden Rossendorf, Germany) using a three-step implantation sequence with ion energies of 3, 1.8, and 0.8 MeV and doses of $10^{15}$, $8 \times 10^{15}$, and $7 \times 10^{15} \text{ cm}^{-2}$, respectively.

Infrared absorption spectra were recorded with a Bomem DA3.01 Fourier transform spectrometer equipped with a globar light source, a 3 $\mu$m Mylar beamsplitter and a liquid-helium-cooled
Si bolometer detector. The temperature of the samples was stabilized within 2 K in the range of 12–300 K in a He exchange-gas cryostat equipped with polypropylene windows. The spectral resolution was 0.1–0.5 cm
superscript 
-1. Polarized light was supplied by a wire-grid polarizer with a KRS-5 substrate.

To estimate the local structure and vibrational properties of the S
subscript Se, defect in wurtzite CdSe, first principle calculations were performed within the framework of the density functional theory (DFT) using the projector augmented wave (PAW) method
superscript 18 and the local density approximation (LDA) to the exchange-correlation energy functional as implemented in ABINIT code.
superscript 19,20 The calculated lattice constants of bulk wurtzite CdSe, \( a = 4.25 \text{ Å} \) and \( c = 6.94 \text{ Å} \), are in good agreement with the corresponding experimental values of 4.31 and 7.03 Å.
superscript 21 To study the defect a \( 2a \times 2a \times c \) hexagonal supercell with periodic boundary conditions comprising eight Cd, seven Se, and one substitutional S atoms was used (Figure 1). A high-precision structure optimization and subsequent calculations were performed using the \( 3 \times 3 \times 4 \) grid of \( k \)-points and an energy cut-off of 40 hartree for the plane wave basis set, whereas an energy cut-off for the fine fast Fourier transform (FFT) grid definition was set to 50 hartree. Phonon modes at the \( \Gamma \) point were calculated using the frozen-phonon approach and density-functional perturbation theory,
superscript 22–24 wherein all possible atomic displacements were considered.

3. Results and Discussion

3.1. General Properties of the IR Lines

Figure 2 shows representative IR absorption spectra recorded at 10 K for as-received CdSe samples provided by different suppliers (see figure caption). As one can see, all samples reveal absorption line(s) at around 271 cm
superscript -1 whose intensity strongly varies from sample to sample. We note that the intensity of the 271 cm
superscript -1 feature does not change significantly within all available CdSe material of the same supplier. In the case of weak absorption (see spectra (a) and (b)), a splitting of the 271 cm
superscript -1 signal into two lines at 270.6 and 271.4 cm
superscript -1 is clearly evident. Stronger absorption broadens the two lines resulting in a single mode at \( \approx 271 \text{ cm}^{-1} \) (see spectra (c) and (d)). We label it as S-line.

The frequency of the S-line is very close to that of tentatively associated with substitutional sulfur in CdSe.
superscript 12–14 A slight mismatch of a few cm
superscript -1 can be well explained by the differences in measurement temperature, spectral resolution, sample orientation, detection technique, etc. The splitting of the 271 cm
superscript -1 line observed in our spectra is consistent with the model of the defect as \( S_{\text{se}} \) as a threefold degenerate vibrational mode of substitutional impurity in wurtzite CdSe should split into a nondegenerate \( A_1 \) and twofold degenerate \( E \) modes of the local \( C_{3v} \) point group.

The frequency of any LVM is inversely proportional to a square root of the mass of the vibrating species. This property offers a straightforward way to unveil the chemical nature of light impurities in semiconductors. This can be done via direct isotope substitution experiments and/or via detection of satellite lines whose intensities match natural isotope abundances of a particular chemical element.

The absorption spectra shown in Figure 2 also reveal additional weak lines at about 264 cm
superscript -1 whose intensity scales up with that of the 271 cm
superscript -1 signal. Sulfur exhibits four stable isotopes: the predominant \( ^{32}\text{S} \) (95.02%), the less abundant \( ^{34}\text{S} \) (4.21%), and two more isotopes with marginally low natural abundances \( (^{33}\text{S}=0.75\% \) and \( ^{36}\text{S}=0.02\% \). The frequency ratio between the 264 and 271 cm
superscript -1 features perfectly matches the value expected for local modes due to the \( ^{34}\text{S} \) and \( ^{33}\text{S} \) isotopes, \( \sqrt{34/32} = 0.97 \). Moreover, from the spectra shown in the figure and the bulk of our experimental data, the intensity ratio between the 264 and 271 cm
superscript -1 features was found to be \( 5 \pm 1 \% \), i.e., in good agreement with that expected from the natural abundances of the \( ^{34}\text{S} \) and \( ^{33}\text{S} \) isotopes (4.43%). Further on, a careful inspection of the spectra reveals that the 264 cm
superscript -1 feature is split into two modes at about 263.6 and 264.4 cm
superscript -1 (see vertical dashed lines). The magnitude of the splitting is very close to that of

Figure 1. Hexagonal supercell containing the local structure of the \( S_{\text{se}} \) defect in CdSe.

Figure 2. Sections of IR absorption spectra obtained at 10 K for as-received CdSe crystals from different suppliers: a) Research Institute of Material Science and Technology, Russia; b) Crystec GmbH; c) Cradley Crystals; and d) SurfaceNet GmbH. Spectra were baseline corrected and vertically offset for clarity. Absorption lines marked by * are due to residual water in the spectrometer.
the major line at 271 cm\(^{-1}\) which gives further support to the suggestion that both features originate from substitutional sulfur.

We note that the IR spectra shown in Figure 2 are prone to three types of distortions: 1) interference fringes with a periodicity of about 2–7 cm\(^{-1}\) due to internal reflections of the IR beam at the polypropylene cryostat windows, 2) broad multi-phonon absorption bands, and 3) a nonlinear detector response affecting strong absorption signals. These obstacles rendered both an identification of the weaker \(^{33}\)S-lines and a more precise determination of the \(^{34}\)S-to-\(^{33}\)S intensity ratio practically impossible.

### 3.2. Polarization Properties

As mentioned already, the \(C_{3v}\) point group of the local environment splits vibrational modes of a substitutional impurity in CdSe into a nondegenerate \(A_1\) and a twofold degenerate \(E\) modes polarized parallel and perpendicular to the \(c\) axis of the crystal, respectively.

Figure 3 shows polarized IR absorption spectra recorded on two CdSe samples with low and high intensities of the \(S\)-lines. Evidently, the 270.6 and 271.4 cm\(^{-1}\) modes assigned to \(^{32}\)S are fully polarized parallel and perpendicular to the \(c\) axis, respectively. The same holds for the 263.6 and 264.4 cm\(^{-1}\) lines associated with \(^{34}\)S. These results support the microscopic origin of the 264 and 271 cm\(^{-1}\) features as due to substitutional sulfur and directly reveal the irreducible representation of each component. That is, the 270.6 and 263.6 cm\(^{-1}\) modes should be associated with the nondegenerate \(A_1\) state, whereas the 271.4 and 264.4 cm\(^{-1}\) modes are due to the twofold degenerate \(E\) state of \(^{34}\)S and \(^{32}\)S, respectively.

### 3.3. \(^{34}\)S Implantation

Implantation with \(^{34}\)S ions was used to directly verify whether sulfur is involved in the defect responsible for the \(S\)-lines. Figure 4 shows IR absorption spectra obtained for two CdSe samples subjected to \(^{34}\)S implantation. The black spectra were recorded before and after implantation. Colored ones are the difference between each pair. Spectra are vertically offset for clarity.

Figure 4. IR absorption spectra obtained for two different CdSe samples implanted with \(^{34}\)S ions. Sample A—\(c\)-plane cut Crystec CdSe, implantation direction and the incoming IR beam are parallel to the \(c\) axis (\(k\parallel c\)); Sample B—(1120)-cut CdSe from the Research Institute of Material Science and Technology, Russia, the implantation direction and the incoming IR beam are aligned along the [1120] axis (\(k\perp c\)). Black spectra were recorded before and after implantation. Colored ones are the difference between each pair. Spectra are vertically offset for clarity.

show the difference between the two. As can be seen, for both samples the implantation does result in a strong increase in the 264 cm\(^{-1}\) signal assigned to \(^{34}\)S at the substitutional Se site. The missing fine-structure of the \(^{34}\)S-line we explain by the line broadening caused by the residual stress due to the implantation damage. Importantly, the intensity of the 271 cm\(^{-1}\) feature associated with the \(^{33}\)S isotope remains marginally weak. These findings provide an ultimate proof for the sulfur-nature of the 264 and 271 cm\(^{-1}\) lines. We note again that “fringes” with a periodicity of about 2–7 cm\(^{-1}\) seen in the spectra are artifacts resulting from internal reflection of the IR beam at the polypropylene cryostat windows.

A careful inspection of the figure reveals that the position of the 264 cm\(^{-1}\) feature in the spectra depends on the measurement geometry. If the incoming light is parallel to the \(c\) axis (\(k\parallel c\)), Sample A) the \(S\)-line slightly blue-shifts with respect to that recorded in the \(k\perp c\) geometry (Sample B). This finding can be conclusively explained on the basis of the polarization properties of the \(S\)-lines (see Section 3.2). In the case of the \(k\parallel c\) geometry, the low-frequency \(A_1\) mode becomes invisible as the electric vector of the incoming light is aligned perpendicular to the \(c\) axis. Because of the substantial broadening of the absorption lines, the \(A_1\) and \(E\) modes cannot be resolved which results in the apparent shift of the \(^{34}\)S-line toward higher frequencies.

### 3.4. Temperature Dependence of the LVMs

Figure 5 shows the frequency shift of the \(^{32}\)S- (red data points) and \(^{34}\)S-line (blue data points) as a function of the temperature.
Table 1. LVMs of the S\textsubscript{Se} defect in wurtzite CdSe for three sulfur isotopes (cm\textsuperscript{-1}).

| Isotope | Theory | Experiment |
|---------|--------|------------|
| $^{32}\text{S}$ | $E$ | 264.3 | 271.4 |
| | $A_1$ | 265.7 | 270.6 |
| $^{34}\text{S}$ | $E$ | 260.7 | – |
| | $A_1$ | 262.1 | – |
| $^{34}\text{S}$ | $E$ | 257.3 | 264.4 |
| | $A_1$ | 258.7 | 263.6 |

Figure 5. Frequency shift of the $^{32}\text{S}$ (red) and $^{34}\text{S}$-line (blue) as a function of temperature. Data were obtained from CdSe crystals purchased from three different suppliers with different $^{32}\text{S}$ and $^{34}\text{S}$ content: ▼ – Research Institute of Material Science and Technology, Russia; ▲ – Cradley Crystals; ● – SurfaceNet GmbH. Solid line is a guide to the eye.

Both features experience a distinct red-shift with increasing temperature. More importantly, the magnitude of the shift is very similar up to the highest temperature measured, corroborating the common microscopic origin of both signals. For the 264 cm\textsuperscript{-1} signal, the broadening of the line and a low signal-to-noise ratio prevented us from any reasonable measurements of the peak position at temperatures above 150 K. For practical use, we note that at room temperature the center of the $^{32}\text{S}$ cm\textsuperscript{-1} mode is located at a frequency of 268.3 cm\textsuperscript{-1}.

3.5. Computational Results

The previous results provide clear evidence for an involvement of sulfur in the defect responsible for the 271 and 264 cm\textsuperscript{-1} lines. Sulfur and selenium are isoelectronic atoms with comparable radii and electronegativity values. Therefore, the substitutional S\textsubscript{Se} in CdSe is a plausible model to be considered theoretically (see Figure 1).

Here, we present our results of first principle calculations on the S\textsubscript{Se} defect in wurtzite CdSe. Obtained values of the vibrational frequencies related to the defect for three sulfur isotopes are listed in Table 1. Generally, local mode analysis by theory is prone to a relatively large systematic error in the vibrational frequencies. This uncertainty in the theoretical estimations can reasonably well explain the observed difference of about 6 cm\textsuperscript{-1} to the experimental values. Taking this scaling into account, we believe that the calculated values are in good agreement with the results of our experimental study. Note also that Talwar et al.\cite{25} have calculated the LVM of S\textsubscript{Se} in cubic CdSe to be located at 264 cm\textsuperscript{-1}, i.e., reasonably close to our values for wurtzite CdSe. The reversed order of the relatively small $E$-to-$A_1$ mode frequency splitting compared between the predicted and experimental data is attributed to the accuracy of our calculations. Summarizing this section, we conclude that the $^{32}\text{S}$\textsubscript{Se} and $^{34}\text{S}$\textsubscript{Se} defect model is consistent with the experimental findings on the 271 and 264 cm\textsuperscript{-1} absorption line.

4. Conclusions

IR absorption spectroscopy and first principle calculations have been applied to identify LVMs of the substitutional sulfur defect, S\textsubscript{Se}, in wurtzite single-crystalline CdSe. The results of polarization and temperature-sensitive measurements performed on nominally undoped as well as $^{34}$S-implanted samples provide conclusive evidence that the $^{32}$S isotope results in two LVMs at 270.6 and 271.4 cm\textsuperscript{-1} (10 K) polarized parallel and perpendicular to the $c$ axis of the crystal, respectively. They were assigned to the nondegenerate $A_1$ and the twofold degenerate $E$ states of the $C_{3v}$ point group. Corresponding signals of the less abundant $^{34}$S isotope were found to occur at 263.6 and 264.4 cm\textsuperscript{-1}, respectively. The concentration of the defect significantly varies between CdSe crystals grown by different manufacturers. Our results highlight that sulfur is an omnipresent impurity in crystalline CdSe which is unintentionally incorporated into the material during the process of crystal growth.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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