

Defect absorption in selenium films by photothermal deflection spectroscopy[★]

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Received: 27 August 2019 / Received in final form: 6 December 2019 / Accepted: 13 February 2020

Abstract. Sub-gap absorption spectra of selenium films are investigated by photothermal deflection spectroscopy. The selenium films are prepared by vacuum evaporation of selenium pellets. Raman spectroscopy reveals that as-deposited films are amorphous, and the films annealed at 100 °C are trigonal crystal. Photothermal deflection spectroscopy is extended to infrared light of 0.31 eV with maintaining high sensitivity, and detects weak absorption at energies below the band gap. Five absorption peaks and tail absorption are observed in selenium films, and the absorption peak energies are 1.32, 1.08, 0.47, 0.41 and 0.34 eV, respectively. These absorption tail and peaks are derived from selenium, and the origin of these absorptions is explained based on the oxygen impurity and the defect structure of the selenium film.

1 Introduction

Selenium (Se) is a semiconductor material consisting of a single element. Applications to high-sensitivity imaging tube and X-ray detection panel utilizing photoelectric characteristics are proceeding [1]. Research is being conducted to improve the performance of these devices. In particular, understanding the photoexcitation process and carrier transport is extremely important. In amorphous semiconductors, the carrier generation and transport processes associated with optical absorption are often influenced by localized states in the band gap. Therefore, it is very important to know the distribution information of localized states and their nature. There are various reports on the defects of amorphous selenium (a-Se) so far [2–12], and the models of charged coordination defects explain several experimental results [2–4,12]. Experimental and theoretical studies are deepening their understanding of a-Se defects [5–12]. In contrast, unclear points remain in the energy and distribution of the level in the gap in Se, and development of a new evaluation method is expected. Photothermal deflection spectroscopy (PDS) is a method for highly sensitive evaluation of sub-gap absorption in semiconductor thin films. The PDS system was extended to the infrared region of 0.31 eV (wavelength 4000 nm, wave number 2500 cm⁻¹) [13]. In this study, the PDS is used to evaluate defect absorption in Se thin films. Thus far, weak tail absorption has been reported for the sub-gap absorption of a-Se [5–8]. The PDS extended to infrared with high sensitivity found new absorption peaks related to

the localized states. It is verified whether the conventional concept of localized states is effective for the absorption peaks. This research provides fundamental insight into defect absorption in Se films, and that understanding leads to further development of photoelectric devices.

2 Experimental details

Se thin films were prepared by vacuum evaporation of Se pellets (purity 99.999%). The substrate temperature was not controlled. Synthetic quartz glass (VIOSIL, Shin-Etsu Chemical), polychlorotrifluoroethylene (PCTFE), and silicon were used for the substrate. The thicknesses of quartz, PCTFE, and silicon were around 0.5, 0.05, and 0.5 mm, respectively. The thickness of the Se films evaluated by optical interference fringes was about 300 nm. Some film samples were placed in a test tube and heat treated at a temperature of about 100 °C in Ar gas. For comparison, bulk samples with a thickness of approximately 1 mm were prepared. Se pellets sandwiched between glass slides were heated in air to form Se plates. The band gaps of as-deposited (AD) and heat-treated (HT) Se films were estimated to be 2.04 and 1.87 eV from the transmittance. These were in good agreement with previous reports [14–16]. Crystalline structure was evaluated by Raman spectroscopy (peekseeker Pek785, Raman systems) with excitation light of 785 nm. The optical absorption spectra were obtained by optical transmittance and the PDS. The transmittance spectra were measured using a spectrometer (UV-1800, Shimadzu). The PDS is suitable for evaluating optical absorption of submicron thick films [17]. The PDS system consisted of an excitation light source and optical detection. Monochromatic light was obtained by a 50 W tungsten-halogen lamp and a monochromator (CM110, Spectral Products). The

[★] Contribution to the Topical Issue “Disordered Semiconductors: Physics and Applications”, edited by Jean-Paul Kleider, Erik Johnson, Rudolf Brüggemann.

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photothermal deflection signal was measured using an optical system consisting of a laser diode with a wavelength of 785 nm, a lock-in amplifier (SR830, Stanford Research), an optical chopper and a position sensor (S3979, Hamamatsu Photonics). To detect a sufficiently strong signal, the sample was placed in a liquid as the deflection medium, perfluorocarbon FC-43. FC-43 has advantages such as transparency in a wide wavelength range of 500 to 4000 nm, stability and less reaction with substances. All structural and spectroscopic measurements were performed at room temperature.

3 Results

Raman spectroscopy is a useful method to know the composition of a substance. Crystalline structure can be evaluated from the Raman spectra of Se thin films. Figure 1 shows the Raman spectra of the as-deposited and thermal annealed Se thin films onto silicon substrate. A relatively broad peak in AD Se films was observed around 250 cm^{-1} . The broad peak disappeared, and a relatively sharp peak appeared around 238 cm^{-1} in HT Se films. According to the literature [18], a broad band around 250 cm^{-1} is caused by the A_1 -symmetry bond-stretching vibrations of the chain fragments and ring-like units that comprise the amorphous Se structure. A sharp peak is identified as composition of the E- and A_1 -symmetry bond-stretching optical modes of trigonal Se. Therefore, it is considered that AD samples are an amorphous phase, and crystallized into a trigonal phase with heat treatment at 100°C .

The optical absorption spectra of semiconductor thin films contain a lot of important information about electronic properties. Interband transition and Urbach tail are noted, and optical absorption related to the localized states in gap is also useful. Figure 2 shows photothermal deflection (PD) spectra of Se bulk, AD Se film, and quartz glass substrate. The Se film was deposited on quartz glass. The intensity of the PD signal was saturated at about 2×10^{-1} . Therefore, in a region smaller than this value, it is proportional to the optical absorption of the sample. In the PDS measurement of the thin film sample on the substrate, absorption of not only the thin film but also the substrate is observed [19]. To reduce the influence of the substrate, a synthetic quartz glass substrate with high purity and low optical absorption over a wide wavelength range from ultraviolet to infrared was used [13]. However, it was difficult to remove the absorption such as OH group, and it was necessary to investigate carefully. The absorption peaks in quartz glass around 0.45 eV (2750 nm) and 0.56 eV (2210 nm) were related to the hydrogen bonding hydroxyl group (OH) [20]. In all energy regions, the signal of the Se film was larger than that of quartz glass. The signal of the Se film increased corresponding to the OH absorption of quartz glass. Therefore, it almost reflects the sub-gap absorption of the Se thin film. In the PD spectra of Se bulk and Se thin film, Urbach tail at $1.6\text{--}2.0\text{ eV}$ and sub-gap absorption below 1.5 eV were observed. In the sub-gap absorption spectrum of the Se thin film, absorption peaks were observed around 1.08 and 1.32 eV . In addition, multiple peaks were observed

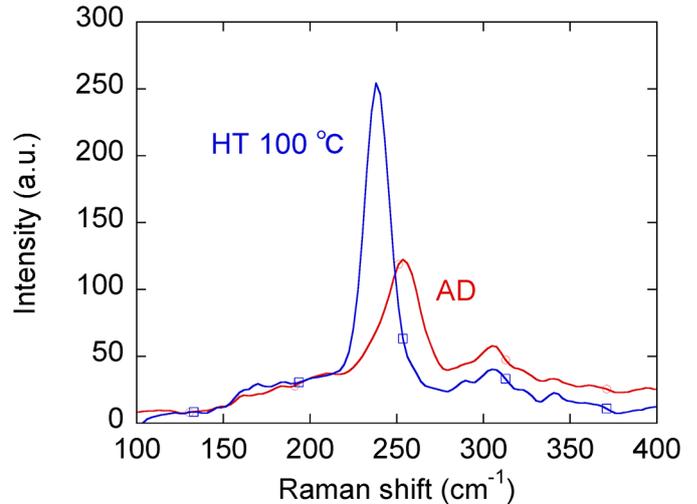


Fig. 1. Raman spectra of as-deposited (AD) and heat treated (HT) Se thin films.

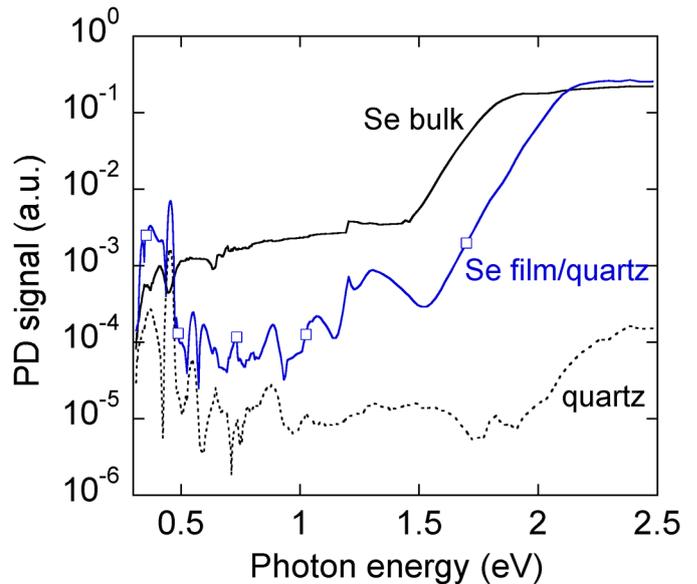


Fig. 2. Photothermal deflection (PD) spectra of AD Se film/quartz, Se bulk, and quartz substrate.

below 0.5 eV . In the limit of the authors' knowledge, there are only a few reports of such absorption peaks in Se films [8]. The effect of the instrument is negated from the result that no absorption peak was observed in the Se bulk sample. To confirm whether this absorption peak is derived from Se, a more transparent substrate was selected.

Figure 3 shows PD spectra of Se bulk, AD Se film, and PCTFE. Se thin films were deposited on PCTFE. As in Figure 2, PD spectra are corresponding to the sub-gap absorption. The OH absorption was not observed, and weak absorption appeared only around 0.4 eV in PCTFE. The intensity of the absorption peak was more than an order of magnitude higher than that of the PCTFE signal. Therefore, the multiple peaks below 0.5 eV , and mid-gap

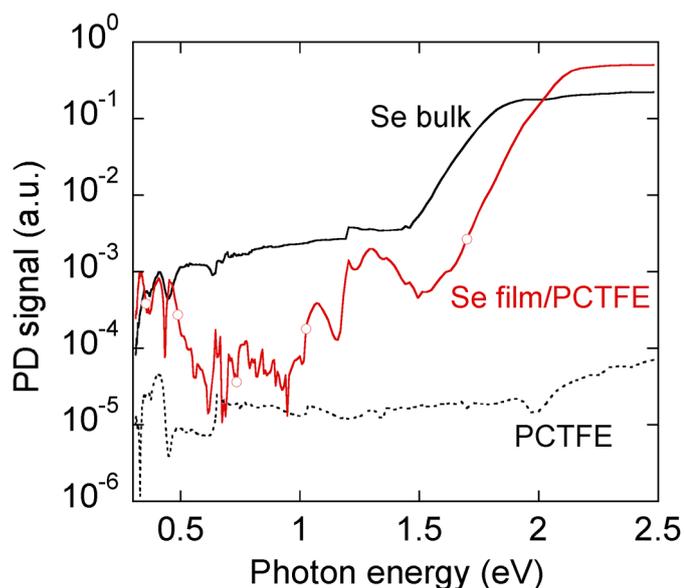


Fig. 3. PD spectra of AD Se film/PCTFE, Se bulk, and PCTFE substrate.

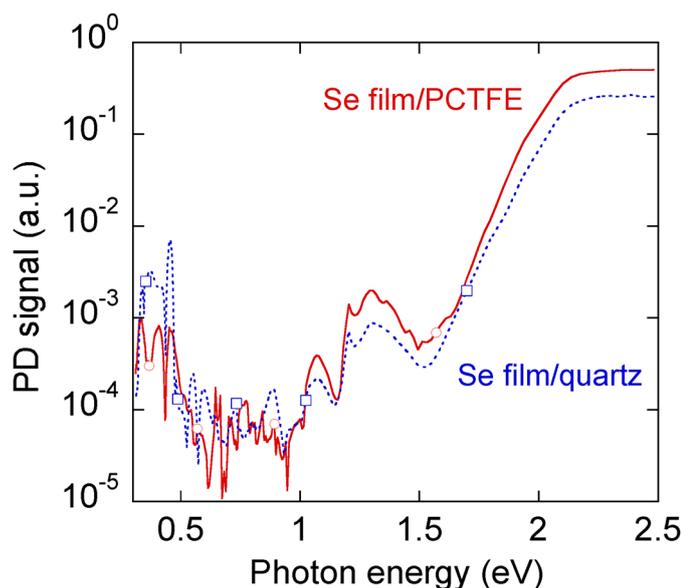


Fig. 4. PD spectra of AD Se film/quartz and Se film/PCTFE.

peaks at 1.08 and 1.32 eV are derived from the Se thin films.

Figure 4 shows the PD spectra of the AD Se thin films deposited on quartz glass and PCTFE. In the Se film/PCTFE spectrum, the peak intensities at 0.45 eV and 0.56 eV decreased greatly. This indicates that the OH absorption of quartz overlapped the Se/quartz spectrum. Therefore, the sample deposited on the PCTFE substrate is suitable for evaluating the sub-gap absorption of Se films.

To evaluate the absorption peak of the sub-gap, separation of peaks assuming a Gaussian distribution

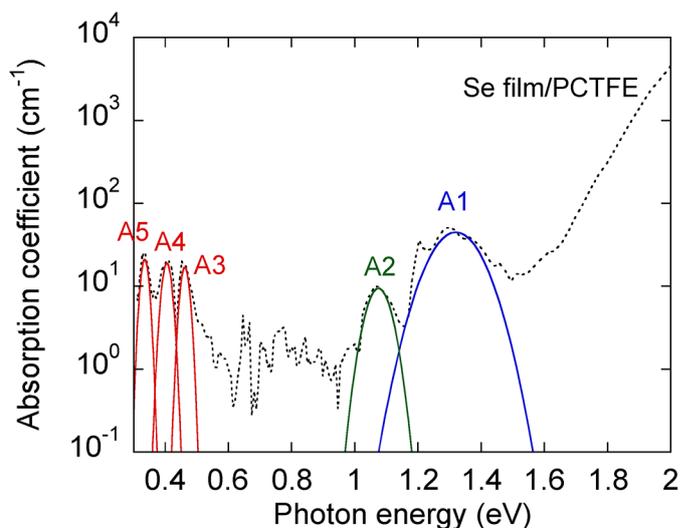


Fig. 5. PD spectra of AD Se film/PCTFE and calculation results based on Gaussian distribution.

was performed. Figure 5 shows the PD spectrum of Se film/PCTFE and the calculation results of five peaks. The five absorption peaks were named A1, A2, A3, A4 and A5 in order from the higher energy, and their peak energies were around 1.32, 1.08, 0.47, 0.41 and 0.34 eV. Although A1 and A2 overlap with tail absorption in the sub-gap, the signal intensity is strong and separable. In the energy region below 0.5 eV, OH absorption of quartz glass is observed. In contrast, the absorption of PCTFE was very small as shown in Figure 3 and confirmed to be derived from Se. The standard deviations of absorption peaks A1 to A5 were estimated to be 0.07, 0.035, 0.015, 0.014 and 0.012 eV, respectively. A1 has the largest signal intensity and standard deviation, and is the main component of sub-gap absorption in Se thin films. The standard deviations from A3 to A5 was less than half that of A1 and A2.

4 Discussion

There are many reports of sub-gap absorption spectra in Se [5–8]. As shown in Figures 2 and 3, tail absorption in 0.5–1.5 eV of Se bulk is the main component of sub-gap absorption in Se. This absorption has been reported to vary depending on the impurity oxygen [5]. In contrast, there are few reports of the absorption peak in Se. An absorption peak at around 1.5 eV has been confirmed in PD spectrum [8], and an absorption peak at around 1.5–1.8 eV has also been reported in the photocurrent spectra [8,11]. The absorption peak energies of A1 to A5 observed in this study are different from previous reports and are new experimental results.

What is the origin of the absorption peak that appears in the sub-gap of Se thin films? First, the possibility of infrared absorption of Se was examined. Se–Se and Se–O vibrational absorption exists at wavelengths longer than 4000 nm (0.31 eV, 2500 cm^{-1}) [21]. In addition, since it does not correspond to the wavenumber of harmonic absorption,

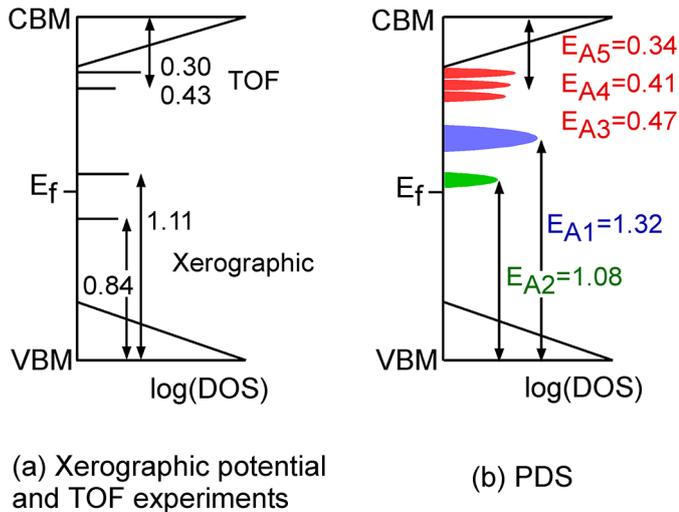


Fig. 6. Schematic density of states as a function of energy for a-Se film. (a) Xerographic potential and TOF transient photoconductivity experiments, (b) PDS. Conduction band minimum, valence band maximum, and Fermi level are denoted as CBM, VBM, and E_f , respectively.

the absorption peaks of $E_{A1} = 1.32$ eV (939 nm), $E_{A2} = 1.08$ eV (1148 nm), $E_{A3} = 0.47$ eV (2638 nm), $E_{A4} = 0.41$ eV (3024 nm) and $E_{A5} = 0.34$ eV (3647 nm) are not molecular vibrations. Therefore, it is reasonable to regard it as absorption peaks caused by electronic transition.

Here, energy levels in band gap were compared with previous reports and PDS experimental results. Figure 6 shows schematic density of states (DOS) as a function of energy in a-Se film. Figure 6a is based on the experimental results of xerographic potential [6] and time-of-flight (TOF) transient photoconductivity [4,12]. The vertical axis is the energy of electrons and the horizontal axis is a logarithm of DOS. The optical gap of a-Se was used as energy difference between the valence band maximum (VBM) and the conduction band minimum (CBM) in Figure 6. In the next section, a band model in Figure 6b based on the PDS results is described. The measured absorption peaks could be a result of the sum of transitions from the VBM to the defect states and from the defect states to the CBM and its tail. To simplify the discussion, the band model from the occupied states to the empty states was considered. The absorption of A1 and A2 corresponds to the optical transition from the VBM to the defect states. Assuming A3 to A5 levels above VBM, the energy position is lower than Fermi energy E_f . Since it is occupied by electrons, optical transition is unlikely to occur. Therefore, the absorption of A3 to A5 was assumed to be optical transitions from the defect states to CBM. Here, we consider shallow levels from CBM and consider them as occupied states. Comparing (a) and (b) in Figure 6, it was found that there is a slight difference in energy, but that it corresponds well. The absorption peak energies of $E_{A5} = 0.34$ eV and $E_{A4} = 0.41$ eV almost agrees with the result of TOF, 0.30 and 0.43 eV from the conduction band edge [12]. The existence of deep states, 0.84 and 1.11 eV from valence band edge, has been confirmed by xerographic

potential [6]. These are roughly correspond to energies of $E_{A2} = 1.08$ eV and $E_{A1} = 1.32$ eV.

What is the nature of defect absorption in a-Se? At first, the influence of impurities was examined. There is a report that the sub-gap absorption intensity in the energy range of 0.6–1.5 eV depends on the impurity oxygen concentration [5]. This experimental result suggests the existence of an oxygen-derived gap state. In the PDS spectra, tail absorption was observed for both Se bulk and Se thin films. Both samples are mixed with oxygen during the preparation process. Therefore, impurity oxygen seems to be the cause of tail absorption.

The cause of peak absorption is considered from the viewpoint of structural defects in a-Se. In microstructure of Se solid, the bond is formed by s^2p^4 electron configuration. As a result, two-fold coordinated covalent bonds and lone-pair (LP) electrons are generated. Therefore, the basic structure of Se is composed of helical chains and stacked rings, and a-Se is considered to be a mixture of entangled chains and distorted rings [11]. Various defect structures related to gap states in Se have been proposed thus far. For instance, there are neutral dangling bonds, charged dangling bonds, impurities, variations of dihedral angle and inter cluster separations [11]. Possible candidates for sub-gap absorption are charged coordination defects in the negative U model [2]. Defects are namely C_1^- a singly coordinated, negatively charged dangling bond and C_3^+ , a three-fold coordinated, positively charged state. Here, character C represents a chalcogen element, subscript a coordination number, and superscript a charged state. However, for charged defects of Se, few studies have confirmed experimentally the energy position and distribution in the band gap [4,12]. Extensive theoretical modeling has been reported to investigate the effect of structural defects on DOS. The concept of the valence-alternation pairs (VAPs) as charged defects is generally accepted [12]. Here is an example of calculating the energy level of the VAPs. Three energies of 0.33, 0.45, and 0.61 eV below conduction band edge are estimated by the difference in the environment of the defect [12]. These values are in good agreement with E_{A3} to E_{A5} in the PDS spectra. In contrast, Benkhedir et al. showed the energy diagrams of occupied defect levels C_1^0 and C_3^0 identified by analyses of TOF transient photoconductivity and steady-state photoconductivity (SSPC) measurements [4]. The energies of C_1^0 and C_3^0 are located at about 0.4 eV and 1.4 eV from the VBM. The energy value of C_3^0 is close to $E_{A1} = 1.32$ eV in the PDS spectra. The defect structure corresponding to $E_{A2} = 1.08$ eV is unknown. A good agreement between experiment and theory shows that weak absorption is a clue to exploring the energy and distribution of defect centers in Se films. The next step is to investigate the behavior of absorption peaks by various treatments.

It was demonstrated to be useful for clarifying the distribution of energy level and localized state in the band gap of Se thin films by using PDS extended to infrared light of 0.31 eV. Understanding the distribution of energy level and localized states of Se thin films is important in science and technology. Advances in the assessment of defect absorption by the PDS help understand these defect structures in Se films.

5 Conclusions

Defect absorption in a-Se films was investigated by PDS extended to infrared light of 0.31 eV. Five absorption peaks of around 1.32, 1.08, 0.47, 0.41 and 0.34 eV, and weak absorption tail of 1–1.5 eV were observed. These absorption peaks and tail contain defect information in the band gap. The PDS results revealed a schematic diagram of the density of states of a-Se thin films, and a good agreement with previous experimental and theoretical results was confirmed. The oxygen impurities in a-Se create weak absorption tail, and charged defects in different environments form multiple absorption peaks. The usefulness of PDS was demonstrated as a method for evaluating the gap states of semiconductor thin films.

This work was supported by Gunma University, Japan.

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Cite this article as: Tamihiro Gotoh, Defect absorption in selenium films by photothermal deflection spectroscopy, *Eur. Phys. J. Appl. Phys.* **89**, 10301 (2020)