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On photoinduced volume change in amorphous selenium: Quantum chemical calculation and Raman spectroscopy

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Hartree–Fock *ab initio* Raman spectra calculations and Raman spectroscopic measurements were carried out on amorphous selenium in order to identify the characteristic vibrational mode due to sigma bonds. Variations in measured peak intensity were observed as a consequence of band gap light illumination. Based on our previous theoretical investigations we originate these intensity variations from photoinduced covalent bond breaking. © *2010 American Institute of Physics*. [doi:10.1063/1.3371813]

I. INTRODUCTION

The amorphous selenium has many applications in infrared, non- and linear optics, in microelectronic engineering, and as x-ray direct image detector for medical use.[1] Most promising field of applications is based on the sensitiveness of a-Se to band gap light illumination showing a plenty of photoinduced phenomena. These photoinduced phenomena are photodarkening, photoinduced volume changes (PVCs), photobleaching, photoamorphisation, photocrystallization, photoinduced anisotropy,[2] etc. Recently Ikeda and Shimakawa[3] performed real time *in situ* measurements of PVC in flatly deposited chalcogenide glasses. They found reversible macroscopic volume expansion during band gap light illumination. Hegedüs *et al.*[4] studied the origin of PVC using tight binding molecular dynamics (TBMDs) simulation. They proposed an atomic scale explanation of the PVC in a-Se. Covalent bond breaking was found in the a-Se network as a consequence of band gap light illumination. To give an experimental evidence for this bond breaking process we carried out Raman spectra experiments.

In the last forty years several Raman spectra measurements have been performed on a-Se. In 1967, as we know for the first time, Lukovsky *et al.*[5] made the identification of fundamental vibrational modes of trigonal, α-monoclinic and amorphous selenium. Experimentally they found six vibrational modes in the Raman spectrum of a-Se at 50, 80, 112, 138, 235, and 250 cm^{-1} wavenumbers. At that time the amorphous selenium was assumed to be constructed of long polymer like chains and rings of eight Se atoms. Based on this assumption the first three wavenumbers were identified as vibrational modes of the eight member selenium rings. The remaining three wavenumbers corresponded to the polymerlike structure. The 235 cm^{-1} wavenumber was linked to the trigonally crystalline Se chain structure. In 2003 the study of Jóvári *et al.*[6] suggested that the a-Se, independently on the method of preparation, contains chain molecules of variable lengths and the dominance of Se_8 rings is improbable. In 1978 Gorman and Solin[7] found characteristic vibrational modes at 80, 110, 132, 234, and 250 cm^{-1} wavenumbers. They identified the 112 cm^{-1} vibrational mode as a Se_8 ring mode. This result was consolidated by Roy *et al.* in 1998.[8] Using extended x-ray absorption fine structure (EXAFS) and Raman spectra measurements they experimentally proved that 112 cm^{-1} mode corresponds to Se_8 rings and ringlike species in the amorphous structure. Later the Raman spectroscopy became a useful tool for the scientist to detect the changes in the structure of a-Se exposed to diverse physical conditions. The effect of pressure,[9,10] mechanical attrition,[11] polarized,[12] and continuous band gap light illumination[13,14] were investigated. A significant and broad Raman peak around 250 cm^{-1} wavenumber and a shoulder at 235 cm^{-1} for a-Se were observed in these experiments.

The theoretical works facilitate the mapping of vibrational modes to structural units of amorphous selenium. In 2001 Demkov and Sankey[15] made a detailed analysis of the properties of Se clusters in zeolites. The geometries, the energetics, electronic and vibrational properties of Se clusters, consisted of 2–12 Se atoms were determined. The electronic properties of two Se crystalline polymorphs, trigonal Se, and α-monoclinic Se, were also calculated. A theoretical study on a glassy structure and infrared/Raman spectra of a-Se were performed by Nakamura and Ikawa in 2002.[16] The vibrational spectra were calculated for 200 different amorphous samples obtained by performing MD simulations for a linear chain of 216 Se atoms. A medium range order was found in the disordered Se chain attributed to the steric hindrance effect. By comparing the polarized Raman spectra of two different random chains (one had medium range order and the other did not) they could identify the 80 cm^{-1} vibrational mode.

In this study our aim was to investigate the microscopic structural changes in a-Se due to band gap light illumination using Raman spectroscopy. First we made *ab initio* Raman

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spectra calculations on a-Se sample grown by MD simulations. Next we measured the Raman spectra of illuminated and nonilluminated a-Se thin films in different time intervals. The differences in the spectra were analyzed next.

This paper is organized in the following way: In Sec. II, we present the theoretical investigation of the Raman spectrum of a-Se. The circumstantial transcription of the a-Se sample preparation is given first. Then we present the details and results of Raman spectra calculations. Section III contains the experimental study of PVC in a-Se with Raman spectroscopy. The results of the first sequence of Raman spectra measurements on non- and light illuminated a-Se thin films are shown in the first subsection. The second sequence of measurements and the detailed analysis of the obtained spectra are presented in the second subsection. We give some conclusions in Sec. IV.

II. THEORETICAL CALCULATIONS

We performed Hartree–Fock (HF) *ab initio* Raman spectra calculations on a-Se to identify the vibrational modes of the sigma bonds in the a-Se network. Our amorphous selenium atomic configurations were prepared by Hegedüs *et al.*[17,18] They followed a "cook and quench" preparation method using TBMDs technique. The 162 atoms were held in a closed box applying three-dimensional periodic boundary condition at the temperature of 5000 K in the 0.6 ps time interval. In this first period the atomic configurations were randomized. Then the temperature was linearly decreased from 700 to 250 K for 4.4 ps to drive the system through the glass transition. The box was opened and during one picosecond the obtained a-Se network has been kept at the 20 K temperature to relax the structure. In this theoretical work we were interested in the mapping peaks in the Raman spectrum to characteristic bonds. For this purpose we considered a characteristic part (no defects) of our amorphous selenium model. Only one individual selenium chain is not sufficient in this study as the effect of the environment need to be included. We took a Se chain and its surrounding four selenium chains and a Se_6 ring, totally 88 Se atoms. Selenium chains were terminated by hydrogen atoms.

We used the GAUSSIAN 03 program package[19] to derive the Raman spectra of a-Se sample. A single point restricted HF calculation has been performed with simple slater type orbital with 3 gaussians (STO-3G)basis set. The obtained Raman spectrum is shown in Fig. 1. There is no expressive peak around 250 cm^{-1} wavenumber as it is a well-known fact that the HF *ab initio* calculations always overestimate the vibrational frequencies.[20] There are two pronounced peaks, one at 224.7 cm^{-1} and a second at 292.7 cm^{-1} wavenumbers. In order to make a comparison to the experimentally measured values we need corrections in the calculations. If we plot the calculated vibrational wavenumbers as a function of covalent bond lengths we can observe an excellent linear correlation. We obtained the best linear fit if $y = -514.8x + 1565.5$. This fit is shown in Fig. 2. Longer bond lengths correspond to smaller vibrational wavenumbers. On base of this correlation we need to increase the average covalent bond length in the atomic configuration from 2.35 to 2.58 Å in order to get more realistic results. It is expected that a significant peak at 250 cm^{-1} wavenumber appears. We repeated the restricted HF calculation on enlarged model. The calculated Raman spectrum is shown in Fig. 3. A wide peak appeared around 250 cm^{-1} wavenumber and a smaller peak at 179.4 cm^{-1} wavenumber. The significant peak around 250 cm^{-1} corresponds to the Se–Se covalent bond. A smaller prepeak at 179.4 cm^{-1} belongs to longer distance between two atoms, which we consider as interchain bonds on the basis of the linear correlation presented on Fig. 2. In the following we concentrate on peaks around 250 cm^{-1} wavenumber.

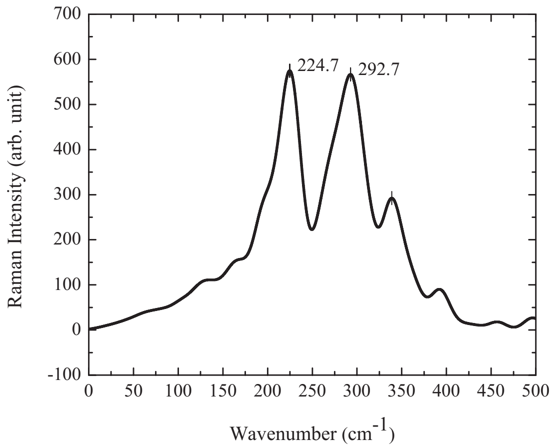

FIG. 1. Calculated Raman spectrum of the a-Se thin film model.

III. EXPERIMENTAL STUDY

We measured the Raman spectra of nonilluminated and illuminated samples to explore the photoinduced atomic level structural changes inside of a-Se. The amorphous samples (having thickness of 0.56 μm) were grown on sapphire substrates at the Gifu University, Japan. The spectra were recorded with a Renishaw 1000 micro-Raman spectrometer using a 785 nm diode laser as excitation source. The laser power was 27 mW and only 20% of it reached the sample. The samples were illuminated with a 488 nm line of an Ar ion laser. To minimize heating of the sample both the

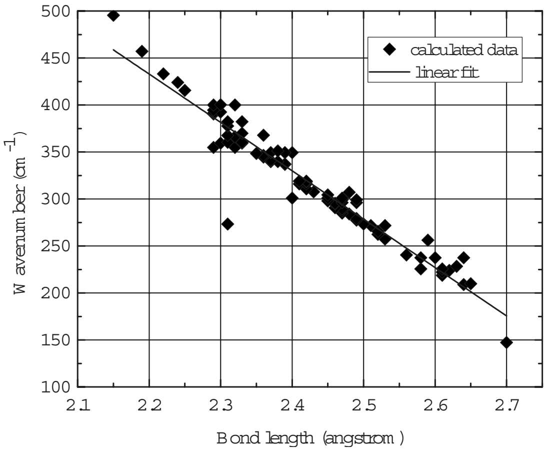

FIG. 2. Calculated vibrational wavenumbers in function of the covalent bonds length (symbols) and best linear fit (solid line).

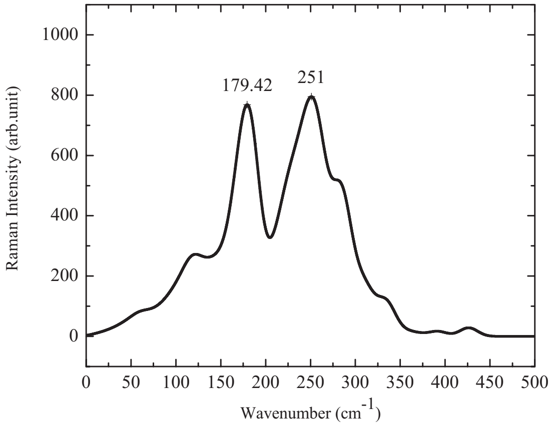

FIG. 3. Calculated Raman spectrum of the enlarged a-Se model sample.

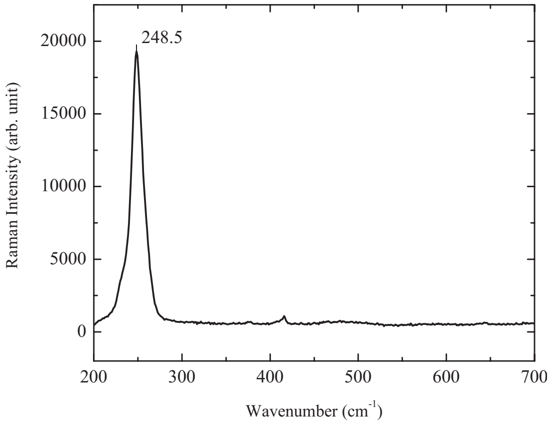

FIG. 5. Measured Raman spectra of nonilluminated a-Se sample.

excitation and illuminating beams were defocused on the sample surface. Two types of measurement sequences were carried out. In the first sequence Raman spectra of the nonilluminated sample was recorded. In the following the sample was illuminated for 10 min. Immediately after switching off illumination the Raman spectrum was measured. After 40 min relaxation a third Raman spectra measurement was accomplished. The time sketch of this first sequence of measurement is presented in Fig. 4(a).

The second turn was a sequential Raman spectra measurement. We performed Raman measurements with one second measurement time within a 300 s time interval. In this period the blue laser was switched on and off twice. From the sequence we can follow changes in the Raman spectra caused by illumination in real time. The time sketch of this second type of experiment is displayed in Fig. 4(b).

A. First sequence of measurements

Before measuring the a-Se sample we recorded the Raman spectrum of the sapphire substrate. We found five significant peaks at 376.8, 414.9, 427.9, 514, and 642.2 cm^{-1} wavenumber, which are in good agreement with other measured data.[21,22]

Our Raman spectrum of a nonilluminated a-Se sample is shown in Fig. 5. We can observe a significant peak at 248.5 cm^{-1} wavenumber. After 10 min blue light illumination the main Raman peak remained the same although a little bit was shifted to 246.5 cm^{-1}, see Fig. 6. Then the sample was let to relax for 40 min and the Raman spectrum was recorded again. The main peak appeared at 247.5 cm^{-1} wavenumber.

A possible reason of displacement of the peak could be the following: during illumination, even if the laser power is low, the sample is warmed up a little bit locally. This local heating causes stress in the amorphous network inducing increase in the spring force and thus the vibrational modes shifts to smaller wavenumbers. When the illumination is switched off the warming up stops, the stress in the network lowers causing the shift in the vibrational modes back to the initial wavenumbers. To detect main effects of light illumination we need to compare the Raman spectra. In Fig. 7 the difference between Raman spectra of the not illuminated sample and that taken immediately after 10 min of illumination with blue light is shown. A significant peak at 248.6 cm^{-1} wavenumber in the positive direction and a

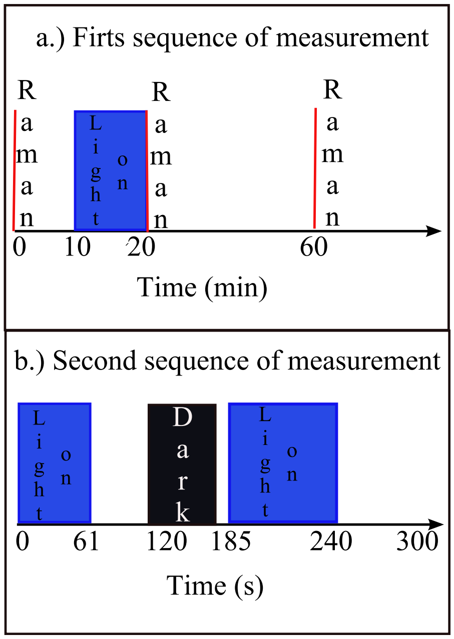

FIG. 4. (Color online) Time sketch of the measurements. (a) First sequence and (b) second sequence.

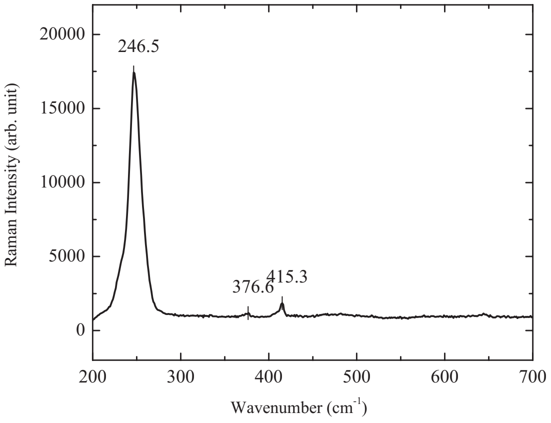

FIG. 6. The a-Se sample was illuminated for 10 min. Immediately after the photoexcitation (488 nm) was switched off the Raman spectrum of the sample was measured. The Raman spectrum is plotted in this figure.

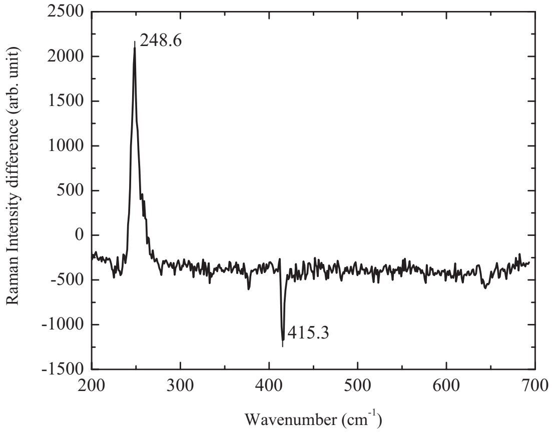

FIG. 7. Difference of Raman spectra between nonilluminated and 10 min illuminated amorphous selenium samples.

smaller peak at 415.3 cm^{-1} wavenumber in the negative direction could be found. This means that a large number of bonds characterized by 248.6 cm^{-1} wavenumber vibrational mode disappears due to band gap light illumination, while bonds having 415.3 cm^{-1} wavenumber vibrational mode are formed. The peak at 415.3 cm^{-1} wavenumber belongs to the sapphire substrate and within this study we do not discuss in more detail its photoinduced changes. We concentrate on the peak in the positive direction which appears at 248.6 cm^{-1} wavenumber. The decrease in Raman intensity is a consequence of blue light illumination and denotes a decrease in the number of covalent Se–Se bonds (bond length is around 2.35 Å). The covalent bond became more longer, we consider it as bond breaking process.

The reversibility of bond breaking process was also proved. If we analyze the difference between Raman spectra measured at the end of 10 min illumination and following after 40 min relaxation we can find a significant peak at 248.6 cm^{-1} wavenumber. The difference of the spectra is presented in Fig. 8. In the absence of illumination bonds with 248.6 cm^{-1} wavenumber are formed. The peak is in the negative direction at 248.6 cm^{-1} wavenumber signifying that the Raman intensity in case of the illuminated sample is less than the intensity of 40 min relaxed sample. The Raman intensity is increasing as the sample is relaxing after light illumination. The increase in Raman intensity denotes a rise in the number of the Se–Se covalent bonds. This means that covalent bonds are being restored in dark. So the bond breaking process caused by the illumination is reversible.

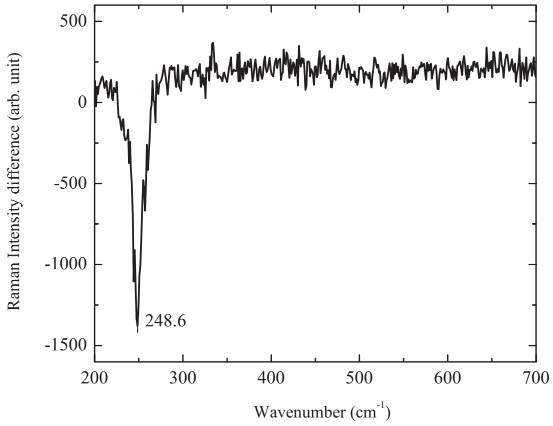

FIG. 8. Difference between the Raman spectra of the 10 min illuminated sample and after 40 min relaxed sample.

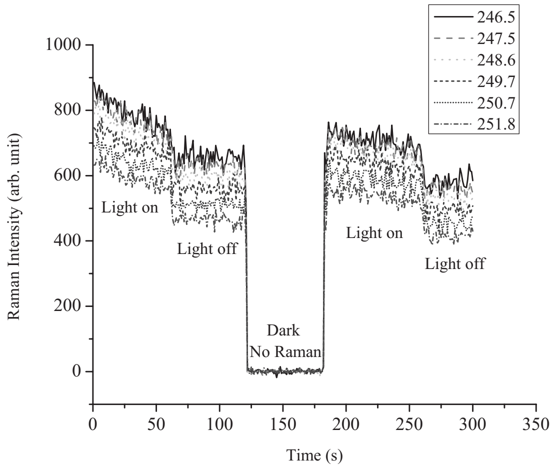

FIG. 9. Time developing of Raman intensities around 250 cm^{-1} wavenumbers.

In our earlier works we performed TBMD simulations on a-Se to investigate the PVCs.[4,23–25] Due to illumination covalent bonds became longer and we consider this effect as bond breakings. Recent Raman measurements give a strong experimental evidence for this photoinduced bond breaking process. Our earlier studies[4] also predicted that photoinduced bond breaking process is reversible in flatly deposited amorphous selenium, which is also supported by our present experimental study.

B. Second sequence of measurements

To have further insight into the photoinduced atomic level structural changes in the a-Se we performed Raman measurements in series one after another. Within a 300 s time interval we switched on and off the excitation (blue light) twice and measured the Raman spectrum of the sample using a 1 s integration time. When we started to record the series the blue laser was turned on ($t_0=1$ s). The blue light illumination held for one minute, then the light was switched off ($t_1=61$ s). After 60 s the excitation laser was switched off, too ($t_2=120$ s). The sample has been kept in dark for one minute. Afterward we switched on the excitation laser and started to record the Raman spectra ($t_3=180$ s). Five seconds later the blue light illumination was also turned on ($t_4=185$ s). Second time the sample was illuminated for 75 s. Then the blue light was turned off ($t_5=260$ s) and the sample relaxed during the time interval of 40 s ($t_6=300$ s).

This second sequence of measurement permits us to follow the variations in Raman intensity of specific vibrational modes in time and so the structural changes caused by the blue light excitation. In Fig. 9 we can explore the changes in Raman intensities around 250 cm^{-1} wavenumbers in time. During light illumination the monotonic decrease in the Raman intensity means that the number of sigma bonds in the amorphous selenium network is lowering. (It should be noted that the steplike lowering of the Raman intensity after switching off the illuminating laser is caused by the break off of the luminescence excited by the blue laser that was superimposed to the whole Raman spectrum as a background.) A slight increase in the intensity can be seen when illuminating the sample with the blue light again after the relaxation ($t_4 = 185$ s) compared to the point where the illumination was switched off ($t_1 = 61$ s). This indicates that bond reformation takes place during the relaxation. Figure 9 confirms the presence of Se–Se covalent bond breaking process and its reversibility.

IV. CONCLUSIONS

We performed a detailed experimental study on photoinduced structural changes in amorphous selenium. In the Raman spectra peaks around 250 cm^{-1} wavenumbers correspond to 2.34 Å covalent bond vibrational modes in the amorphous selenium. As the Raman intensity is varying in time due to illumination we conclude that a large number of covalent bonds break and after stopping the illumination they are formed again. Our Raman spectrum measurement gives a strong experimental evidence for this photoinduced bond breaking process which had been predicted earlier by us.[4,23,24]

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