physica status solidi

pss

www.pss-journals.com

reprint

WILEY-VCH

Phys. Status Solidi C **8**, No. 9, 2789–2791 (2011) / **DOI** 10.1002/pssc.201084144

physica status solidi pss c
www.pss-c.com
current topics in solid state physics

Photoinduced bond breaking in a-Se: Raman spectroscopic study

R. Lukacs[*, 1], **M. Veres**[2], **K. Shimakawa**[3], **and S. Kugler**[1, 4]

[1] Department of Theoretical Physics, Budapest University of Technology and Economics, 1118 Budapest, Hungary
[2] Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, Budapest, Hungary
[3] Department of Electrical and Electronic Engineering, Gifu University, Gifu 501-1193, Japan
[4] Joint Research Center of High-Technology of Tokyo Polytechnic University, Tokyo, Japan

Received 3 October 2010, accepted 4 February 2011

Keywords chalcogenides, a-Se, Raman spectroscopy, molecular dynamics

---

* Corresponding author: e-mail lukacsr@phy.bme.hu, Phone: +36 1 463 2691, Fax: +36 1 463 3567

In flatly deposited a-Se films photoexpansion has been found due to covalent bond breaking during the electron excitation process, and simultaneously photocontraction due to inter-chain bond formation in the case of hole creation. Determination and explanation of the microscopic photoinduced changes in amorphous selenium structure was the purpose of this investigation. For this purpose Raman spectra measurements have been carried out on flatly amorphous selenium (a-Se). Reversible covalent bond breaking process was found as a consequence of band gap light illumination in the experiments. Our bond breaking model obtained using Molecular Dynamics simulations has been confirmed experimentally by Raman spectroscopy.

1 Introduction

Chalcogenide glasses are materials in amorphous phase which contain one or more of the chalcogenide elements S, Se and Te. They represent a significant part of the most researched photonic materials. Chalcogenide glasses show a variety of photoinduced effects during band-gap light illumination, like photoinduced volume change [1-2] (expansion or contraction), photodarkening, photobleaching, photodensification, etc. Recently, Ikeda and Shimakawa [3] published their experimental results on photo induced volume change on flatly and obliquely deposited a-As_2Se_3. Flatly deposited sample showed photoinduced volume expansion while the obliquely deposited one shrank during the illumination. In flatly deposited a-Se (which is the widely used model material for chalcogenide glasses) films photoexpansion has been found due to covalent bond breaking during the electron excitation process, and simultaneously photocontraction occurred due to inter-chain bond formation in the case of hole creation [4, 5].

In obliquely deposited amorphous selenium samples reversible and irreversible volume contraction was found as a consequence of reversible and irreversible covalent bond breaking. Irreversible volume contraction was also reported caused by irreversible covalent bond creation [6]. The obliquely deposited a-Se samples were more responsive to the illumination than the flatly deposited ones because of larger number of degrees of freedom due to voids. These simulations pointed out that the microscopic covalent bond breakings and creations during illumination with band gap light induce the macroscopic expansion or contraction of the material. This bond breaking model based on results of Molecular Dynamics simulations has been confirmed experimentally by Raman spectroscopy [7]. In section two we will present in details our experimental results. Conclusions are summarized in the third section.

2 Raman spectroscopic measurements

The Raman spectra of illuminated and non-illuminated amorphous selenium samples were measured to explore the photoinduced atomic level structural changes inside the samples. The a-Se thin films (having thickness of 0.56 µm) were grown on sapphire substrates by K. Shimakawa at Gifu University, Japan. The films were prepared from six-nine purity Se ingot. They were deposited by the conventional thermal evaporation method in vacuum ($\sim 1\times10^{-6}$ Torr) at room temperature. The films were deposited at normal incidence to the substrate. 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 but 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 excitation and illuminating beams were defocused on the sample surface.

Before measuring the a-Se sample the Raman spectrum of the sapphire substrate was recorded. The spectrum is shown in Fig. 1. We found a large peak at 414.9 cm^{-1} and four other peaks at 376.8 cm^{-1}, 428 cm^{-1}, 514.9 cm^{-1} and 642.2 cm^{-1} wavenumber, which are in good agreement with other measured data [8, 9].

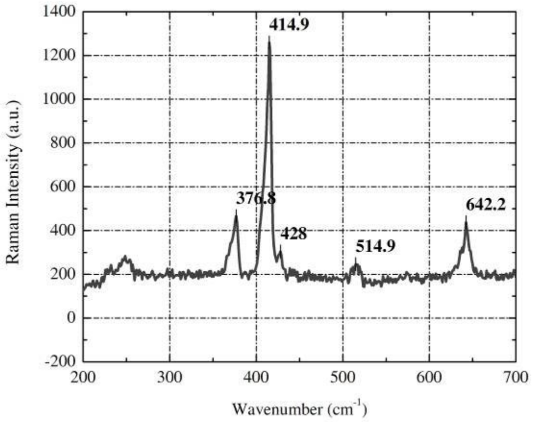

Figure 1 Raman spectrum of the sapphire substrate.

The Raman spectrum of the non-illuminated sample was recorded next. A significant peak was observed around 248.6 cm^{-1} wavelength, see Fig. 2. Other experiments reported also a significant and broad Raman peak around 250 cm^{-1} wavenumber [10-12].

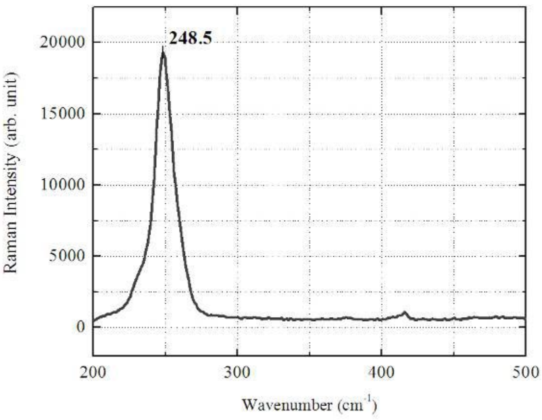

Figure 2 Raman spectrum of non-illuminated a-Se sample.

In the following the sample was illuminated with the Ar ion laser for 10 minutes. Immediately after switching off the illumination the Raman spectrum was recorded. After 40 minutes relaxation a third Raman measurement was accomplished. Figure 3 shows the difference between Raman spectra of the non illuminated sample and that taken immediately after 10 minutes of illumination with the Ar ion laser.

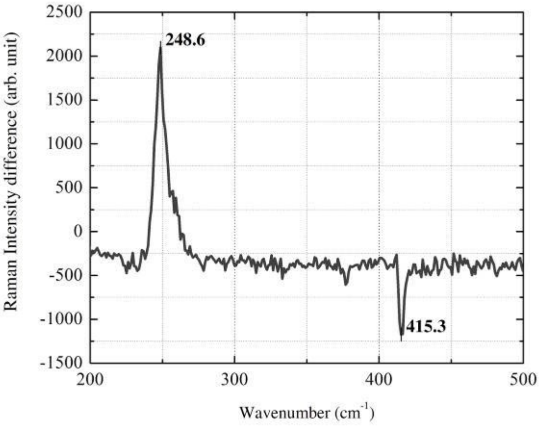

Figure 3 Differential Raman spectrum of the non-illumi-nated and illuminated for 10 minutes a-Se samples.

A significant peak at 248.6 cm^{-1} wavenumber in the positive direction and a small peak at 415.3 cm^{-1} in the negative direction were found. The peak at 415.3 cm^{-1} belongs to the sapphire (see Fig. 1) and within this study we do not concentrate on it. The peak at 248.6 cm^{-1} corresponds to the Se-Se covalent bonds. According to our calculations this peak position corresponds to bond length of 2.35 Å. The decrease in Raman intensity is a consequence of blue light illumination and denotes a decrease in the number of covalent Se–Se bonds. The covalent bonds became more longer, we consider it as bond breaking process.

Raman measurements also prove the reversibility of bond breaking process. If we analyze the difference between Raman spectra measured at the end of 10 minutes illumination and following after 40 minutes relaxation we can find a significant peak at 248.6 cm^{-1} wavenumber in the negative direction. This differential spectrum is presented in Fig. 4.

Figure 4 shows that 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 when the illumination is switched off. So the bond breaking process caused by the illumination is reversible. In our earlier works we performed Tight Binding Molecular Dynamics simulations on a-Se to investigate

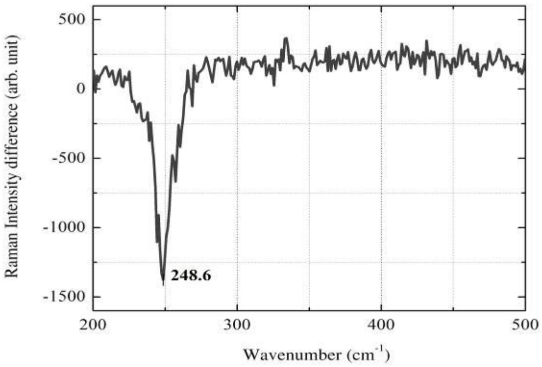

Figure 4 Differential Raman spectrum of a-Se sample taken after10 minutes illumination and 40 minutes relaxation respectively.

the photoinduced volume change [4-6]. Due to illumination covalent bond breakings were found and the samples expanded macroscopically. Our earlier theoretical studies also predicted that photoinduced bond breaking process is reversible in flatly deposited amorphous selenium. This recent Raman spectroscopic result is also experimental evidence to the theoretical prediction.

3 Conclusions

We performed a detailed experimental study on photoinduced structural changes in flatly deposited amorphous selenium thin films. In the Raman spectra the peaks around 250 cm^{-1} wavenumbers correspond to 2.34 Å covalent bonds vibrational modes in the amorphous Se. As the Raman intensity varies 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 spectroscopic measurement gives a strong experimental evidence for this photoinduced bond breaking process which had been predicted earlier by us.

Acknowledgements This work was supported by the Japanese-Hungarian intergovernmental project (Project No: JP-20/09). We would like to thank to K. Kohary (University of Exeter, UK) and J. Hegedüs (University of Helsinki, Finnland) for valuable discussions.

References

[1] Ke. Tanaka, Solid State Mater. Sci. **1**, 567 (1996).
[2] K. Shimakawa, A. Kolobov, and S. R. Elliott, Adv. Phys. **44**, 475 (1995).
[3] Y. Ikeda and K. Shimakawa, J. Non-Cryst. Solids **338-340**, 539 (2004).
[4] J. Hegedüs, K. Kohary, D. G. Pettifor, K. Shimakawa, and S. Kugler, Phys. Rev. Lett. **95**, 206803 (2005).
[5] J. Hegedüs, K. Kohary, and S. Kugler, J. Non-Cryst. Solids **352**, 1587 (2006).
[6] R. Lukacs, J. Hegedüs, and S. Kugler, J. Appl. Phys **104**, 103512 (2008).
[7] R. Lukacs, M. Veres, K. Shimakawa, and S. Kugler, J.Appl. Phys **107**, 073517 (2010).
[8] Y. Wang, S. Liu, G. Peng, S. Zhou, and J. Xu, J. Cryst. Growth **274,** 241 (2005).
[9] G. Wang, H. Zuo, H. Zhang, Q. Wuc, M. Zhang, X. He, Z. Hu, and L. Zhu, Mater. Design **31,** 706 (2010).
[10] V. V. Poborchii, A. V. Kolobov, and K. Tanaka, Appl. Phys. Lett. **72**, 1167 (1998).
[11] K. Okano, I. Saito, T. Mine, Y. Suzuki, T. Yamada, N. Rupesinghe, G.A.J. Amaratunga, W.I. Milne, and D.R.T. Zahn, J. Non-Cryst. Solids **353**, 308 (2007).
[12] R. E. Tallman, B.A. Weinstein, A. Reznik, M. Kubota, K. Tanioka, and J.A. Rowlands J. Non-Cryst. Solids **354**, 4577 (2008).