

# Photoinduced volume change in chalcogenide glasses

(Ph.D. thesis points)

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## Background

The chalcogenide glasses are one of the most researched materials of this century, because they have several important applicable properties. The chalcogenide glasses are amorphous semiconductors containing one or more chalcogenide elements (S, Te and Se). They are often used in infrared optics (ex. optical fibres) as they are transparent into the far infrared and show third order optical nonlinearities. The most interesting and most researched property of chalcogenide glasses is that they are sensitive to band-gap light illumination and showing as a consequence a plenty of photoinduced phenomena like photoinduced volume change, photodarkening, photobleaching, photoamorphisation, photocrystallisation etc. The DVD technology is based on the photoamorphisation/crystallisation phenomena of the chalcogenide glasses. Recently the amorphous Selenium is applied in X-ray detectors in medical devices.

The photoinduced volume changes in chalcogenide glasses were in the focus of my research. I wanted to explore this phenomenon from different theoretical and experimental approaches. My work was based on the following experiments: In 2004 Y. Ikeda and K. Shimakawa measured *in situ* the photoinduced volume changes of amorphous *Se* and  $As_2Se_3$ . They investigated two types of samples. One part of the samples was grown along to the normal of the substrate (flatly deposited

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samples). These samples expanded during band-gap light illumination. The other samples were deposited in an angle of  $80^\circ$  to the normal of the substrate (oblique samples). In these cases the samples shrank while they were illuminated by light. The samples chemically were the same so one possible origin of the distinct behaviour could be the differences in their structures. Experimentally showing structural differences in amorphous samples is a hard task. So I approached the problem from theoretical point of view with the tools of computer simulations. Nowadays the fast and efficient supercomputers make possible the atomic scale study of the material. One can find several methods for its realisation in computational physics.

The photoinduced volume changes of flatly deposited chalcogenide glasses were studied by József Hegedűs. He presented his results in his doctoral thesis titled "Computer simulation of growth and photo-induced phenomena". One part of my research is the continuation of his work.

## **Goals**

My main objective was to explain the different photoinduced volume changes of flatly and obliquely deposited chalcogenide glasses. The model material of chalcogenide glasses is the amorphous Selenium (a-Se), in my study I have concentrated on this material. If we fully

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understand the photoinduced volume change of amorphous Selenium, this will enormously improve the accurate description of the photoinduced volume changes in complex chalcogenide glasses (ex.  $Ge_2As_2Te_5$ ).

For this purpose as a first step I investigated the photoinduced volume changes of obliquely deposited amorphous Selenium thin films. I prepared several a-Se samples with different angles of incidence by Molecular Dynamics simulations. I made a detailed investigation of the structure of oblique samples to understand the mechanism of the photoinduced volume changes. Within I determined the radial distribution function and the density of the different samples. Next I calculated the coordination number distribution, the ring size distribution of the samples and the size of voids within them.

Secondly I modelled the photoinduced volume changes of oblique a-Se samples with new Molecular Dynamics simulations. Following I analysed the different simulation results on macroscopic and microscopic level.

My next purpose was to give experimental evidence for the results of the simulations. First I calculated theoretically Raman spectra of a-Se samples to a better understanding of the experimental outcomes. Then I carried out Raman spectroscopic measurements on amorphous Selenium samples grown on sapphire substrate. The samples were illuminated for different time intervals with a 488 nm wavelength laser beam.

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To understand the photoinduced volume changes of amorphous Selenium is important to investigate the electronic structure. Using quantum chemical calculations I analysed the charge accumulation on Se atoms.

## **Methods**

I applied mostly the method of Molecular Dynamics simulation. With Molecular Dynamics we could follow in space and time the trace of the atoms by solving the Newton differential equations for each atom. This method made possible the atomic scale study of amorphous Selenium. In the simulations of thermal evaporation growth process I calculated the atomic interactions with a classical empirical three-body potential. I solved the differential equations with the velocity Verlet algorithm. I chose the timestep to be 1 fs. The simulations were carried out using computer resources provided us by Tokyo Polytechnic University. An average growth simulation ran for a month.

In the simulations of photoinduced changes I described the interactions between the atoms with a Tight-Binding model. If a-Se absorbs a photon an electron-hole pair will be created which became separated in space on femtoseconds time scale. Due to this finding I modelled the band-gap light illumination in two steps. In first type of simulations I modelled the electron excitation process by placing one electron from the Highest Occu-

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pied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). In the second simulations I modelled the hole creation process by removing definitely one electron from the HOMO. I wrote several programs in C and in Matlab to analyse the results of the simulations.

I calculated the charge accumulation and Raman spectra of amorphous Selenium with Hartree-Fock *ab initio* method using the GAUSSIAN 03 program package.

I carried out the Raman spectroscopic measurements on a Renishaw 1000 micro raman spectrometer.

## **New scientific results**

- I. I prepared several amorphous Selenium samples with average angles of  $0^\circ$ ,  $20^\circ$ ,  $45^\circ$ ,  $60^\circ$  between the normal to the substrate and the direction of the randomly directed incidence atoms using Molecular Dynamics simulations. I found decreasing density in function of the increasing angle of incidence. Applying the Voronoy-Delaunay method I have shown that in the obliquely deposited samples appear more and large voids causing decrease in density [1, 2].
- II. Using Tight Binding Molecular Dynamics simulations I have studied the photoinduced volume changes in obliquely deposited amorphous Selenium samples. I established that the obliquely deposited sam-

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ples containing voids show a wider spectrum of photoinduced structural changes than the flatly deposited ones, like: covalent and inter-chain bond breakings and formations, chain slips, ring formations, reversible and irreversible photo contraction and expansion. I pointed out that the photoinduced volume contraction is caused by the void size reduction [1, 2, 3].

- III. With Hartree-Fock *ab initio* method I calculated the Raman spectrum of amorphous Selenium. I found linear correlation between the Se–Se covalent bond length and their vibrational mode wavenumbers. I have pointed out that to longer bond lengths correspond smaller vibrational mode wavenumbers [4].
- IV. I measured and compared the Raman spectra of illuminated and non-illuminated amorphous Selenium samples. I observed that the intensity of the spectra is varying due to illumination. I concluded that during illumination a part of the covalent bonds break and in the absence of the illumination the covalent bonds are restored causing intensity variation in the spectra [4].
- V. I proposed a phenomenological model to describe the dynamics of the photoinduced volume change in chalcogenide glasses. Applying this model I describe both the kinetics of the photoinduced volume expansion due to illumination and the kinetics of



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relaxation following the switch off the illumination. I give a quantitative estimation for the local conversion rate of structural units responsible for the effect into the expanded states [5].

- VI. I created a simple model for the calculation of charge accumulation in amorphous Selenium chains depending only on bond angles. I tested the quality of the model by Hartree-Fock *ab initio* calculations [6].
- VII. I calculated the charge accumulation on coordination defects of amorphous Selenium by Tight-Binding and Density Functional Theory methods. On Selenium atoms with coordination number three I found positive charge accumulation and on Se atoms at the ends of the chains appeared negative charge accumulation. This results suggests that there is no need for the phonon-electron interaction to appear negative charge accumulation on the ends of Selenium chains [7].

## References

- [1] S. Kugler, J. Hegedűs and **R. Lukacs**  
*On photoinduced volume changes in chalcogenide glasses*  
J. Optoelectr. and Adv. Mater. **9**, 37 (2007).  
Cited by:  
i. P. Ichev et al. J. Phys: Conference Series **113**, 012017 (2008).  
ii. M. Popescu et al. J. Optoelectron. and Adv. Mater. **10**, 2616 (2008).
- [2] **R. Lukacs**, J. Hegedűs and S. Kugler  
*Structure and photo-induced volume change of obliquely deposited amorphous Selenium*  
J. App. Phys. **104**, 103512 (2008).  
Cited by:  
i. A. Pedone J. Phys. Chem. C **113**, 20773 (2009).
- [3] **R. Lukacs** and S. Kugler  
*Photoinduced volume changes in obliquely deposited  $\alpha$ -Se*  
Phys. Stat. Sol. C **7**, 509 (2010).
- [4] **R. Lukacs**, M. Veres, K. Shimakawa and S. Kugler  
*On photoinduced volume change in amorphous Selenium: Quantum chemical calculation and Raman spectroscopy*  
J. App. Phys. **107**, 073517 (2010).
- [5] **R. Lukacs**, S. D. Baranovskii, P. Thomas and F. Gebhard  
*To the kinetics of photoinduced volume changes in*

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*chalcogenide glasses*

J. of App. Phys. **103**, 093541 (2008).

Cited by:

- i. K. Tanaka and M. Mikami J. Optoelectron. and Adv. Mater. **11**, 1885 (2009).

[6] **R. Lukacs** and S. Kugler

*A simple model for the estimation of charge accumulation in amorphous Selenium.*

Chem. Phys. Lett. DOI:10.1016/j.cplett.2010.06.037 (2010).

[7] **R. Lukacs**, J. Hegedűs and S. Kugler

*Microscopic and macroscopic models of photo-induced volume changes in amorphous Selenium*

J. of Mater. Sci.: Mater. in El. **20**, 33 (2010).