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STRUCTURAL CHANGES IN FULLERITE C_{60} INDUCED BY LIGHT-IRRADIATION AND AMBIENT OXYGEN

Summary of PhD thesis

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The work is performed in the Daugavpils University, Department of Physics and in the University of Latvia, Institute of Solid State Physics from 01.11.1998 to 01.02.2004.

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Structure of the work

The promotion work is composed of introduction, review of literature, aim and tasks of the study, description of the objects and methods, section of results and discussion, list of references, summary of results and conclusions as well as the list of author's publications. The supplements include the copies of papers on the promotion theme published in international journals.

Bibliography: 46 pages, 35 figures, 2 tables, 44 references.

Actuality of the study

The promotion work is devoted to investigation of photo-induced polymerization in fullerite C_{60} single crystals. Studies concerning the fullerene polymers are of interest for possible applications of fullerite in lithography and holography as well as for obtaining hard and ultrahard phases of fullerite.

It follows from the review of published data that the phenomenon of photopolymerization is well-known since 1993 and general conception about the nature of photopolymerization is established during 1993 –1995, however, numerous substantial problems remain unsolved.

To clear up the conditions and mechanisms of photopolimerization, it is necessary to perform systematic investigations of the wavelength dependence and kinetics of photopolymerization, to ascertain the effect of temperature on photopolymerization, to assess the thermal stability of photopolymers, find out the effect of absorbed gases and search the effects of polymerization-induced stresses and their role in photopolymerization.

The aim of the present work is to investigate the behaviour of photo-induced polymerization in fullerite C_{60} single crystals under irradiation with visible and ultraviolet light by microindentation, dislocation mobility and atomic force microscopy methods.

Content of the work

The introduction includes the history of fullerene discovery, more important research results and applications, brief description of physical, mechanical, chemical properties and photoinduced structural transformations in fullerite C_{60}. Further sections contain the aim and tasks of the doctoral study, the description of the fullerite single crystals, their characterization by X-ray diffraction and Raman spectroscopy, description of the microindentation and dislocation mobility methods, characterization of the experimental procedures and light sources used in the present study.

The section of results and discussion includes 6 paragraphs devoted to general description of the behaviour of photoinduced polymerization (5.1), and investigation of wavelength dependence (5.2), kinetics of photopolymerization (5.3), effects of temperature (5.4), air exposure (5.5) and mechanical stresses generated during photopolymerization (5.6).

Investigations were performed on high purity (99.95%) fullerite C_{60} single crystals grown in the Institute of Physical Energetics, Latvian Academy of Sciences. The crystals are characterized by a low density of grown-in dislocations ($5x10^3$ cm^{-2}). The surfaces are free from oxides and contaminants, their size and smoothness fit the contributions for mechanical and optical measurements.

A row of eksperiments was performed in the doctoral study to clear up the essential conditions of photopolymerization:

- the wavelength dependence of photopolymerization was elucidated. The investigations in a broad wavelength range (150 nm – 900 nm) were performed for the first time. The measurements of the optical absorption spectra showed that the fullerite is transparent for the infrared light and the absorption edge is about 720 nm (1,7 eV). It has been found that the photopolymerization occurs under illumination with visible and ultraviolet light at the wavelength λ<800 nm that corresponds to photon energies above 1,55 eV. The threshold photon energies correspond to referred data for exciton band in fullerite. Therefore, the photopolymerization occurs in the fundamental absorption region of fullerite including the sub-band gap photon energies, which correspond to energies of photogenerated excitons in fullerite. It has been established that the efficiency of polymerization increases with increasing the wavelength.
- the temperature limits of photo-induced polymerization were cleared up. The photopolymerization was found to occur in the face-centered-cubic phase of fullerite in the temperature range of 260-400K. The obtained result is in agreement with the referred data of other authors.
- the thermal stability of fullerite photopolymers was studied. It has been found, that the temperature of its depolymerization, above which the fullerite returns in its pristine state, is 440- 470K depending on heating rate. The result, indicating possible formation of two phototransformed phases of fullerite with different thermal stability, was obtained for the first time.

- it has been found that detectable photo-induced changes in hardness appear at the dosage of few tens of photons per fullerene molecule, while the saturation stage of polymerization is reached at hundreds of photons per fullerene molecule. The result shows that fullerite single crystals exhibit higher light sensitivity compared to polycrystalline fullerite films. For the fullerite films, the saturation is known to be reached at the dosage of about 10^4 photons per fullerene molecule.
- the depth-evolution of photopolymerized phase was investigated for the first time. The results confirm that the thickness of photopolymerized layer is limited by the light penetration depth in fullerite. However, the difference in polymerization behaviour on the surface and in the deeper layers is observed giving evidence for the effect of air exposure.

Generally, the obtained results can be explained by the well-known model of linear polymerization based on photochemical [2+2] cycloaddition reaction. The model was proposed in 1993. In this model, the neighbour fullerene molecules are optically excitated, that makes possible creation of cross-linking C=C bonds and leads to formation of covalently bonded fullerene dimers or larger chains in the molecular lattice of fullerite. Such a reaction is possible when two fullerene molecules approach each other, are oriented in a needed position and simultaneously activated. However, the possibility of fulfilling these conditions is comparatively low and, therefore, a comparatively large number of photons per fullerene molecule for initiation of photopolymerization is needed. It should be taken into account that the living time of activated state is very short and the coincidence of activated positions can be ensured only under conditions when fullerene molecules freely rotate. This freedom the molecules have only in the face-centered –cubic phase. Because of this the photopolymerization is possible at temperatures above the transition temperature to the face-centered –cubic phase (260 K), as it was observed experimentally. The experiments confirm that the efficiency of polymerization increases with increasing the wavelength as it was predicted by the [2+2] reaction model.

Earlier research is based on the conception about fullerene C_{60} dimers (or C_{120}) as the main element of fullerite photopolymer. This idea is partially confirmed by our studies of photopolymerization kinetics and thermal stability of photopolymer. It has been found that the typical phase of fullerite with the hardness of 450 MPa and depolymerization temperature of 470 K is formed during the photopolymerization. The This phase is recognized as the well-known fullerite polymer consisting of fullerene dimers.

Novelty of results

Important novelty of the present work is the evidence for the existence of a new phototransformed phase. This phase is formed at temperatures below 320K and is characterized by a markedly higher hardness (650-1000MPa) that approaches the hardness of the polymer phases obtained under high pressure – high temperature treatment. This new phase has lower depolymerization temperature (320K) compared to that for well-known phase consisting of C_{120}. It disobeys the typical for all-carbon polymers rule that the phases with a higher hardness have a higher degree of polymerization and higher depolymerization temperature. The experiments show a converse result giving rise for question whereas the hard photopolymer has the all-carbon composition. This doubt is deepened by the fact that the formation of hard photopolymer is promoted by saturation the fullerite with oxygen during its maintenance in air atmosphere. Besides, the hard polymer is localized in a very thin near-surface layer (up to 0.5 μm), which is subjected to air exposure. These considerations allowed us to advance a novel model of C_{60} dimer, in which oxygen is involved in the photoinduced [2+2] reaction. This dimer is connected by an oxygen bridge and a single carbon bond. Similar model was proposed earlier for description of ageing processes in fullerite where the mass-spectra show the presence of $C_{120}O$. Thus, the results of the present study motivate the idea of the existence of two phototransformed phases. In general, the obtained results can be explained by the photochemical [2+2] reaction, in which depending on the conditions of the experiment, all-carbon fullerene dimers (C_{120}) or $C_{120}O$ dimers are created. In the later case C_{60} molecules possibly are connected by an oxygen bridge and a single carbon bond.

Investigations of the dislocation mobility in the wavelength range of UV light with λ= 147 nm give evidence for a specific mechanism of phototransformation. The result was unexpected because the phototransformation in air atmosphere was observed not only inside the light irradiated area but also outside of it including the opposite side of the crystal. Obviously, the result points to participation of gaseous atmosphere in the photochemical transformation. At the 147 nm wavelength, the photon energy exceeds the threshold of 5,17 eV for dissociation of ambient O_2 and formation of ozone and its reaction with fullerite becomes possible. It is well-known that ozone reacts with fullerite with formation of polymerized fullerite/oxygen structure (ozopolymer). It has been concluded, that the major role in the photopolymerization under irradiation with UV light at $\lambda \leq 147$ nm in air atmosphere plays the photogeneration of ozone and its reaction with fullerite.

Much attention in the study is devoted to the role of polymerization induced stresses. The systematic study of the stress effects is performed for the first time. The formation of covalently bonded fullerene dimers in a molecular lattice of fullerite creates internal and long range stresses. There has been reported a change of the lattice constant by about 2 %, that creates significant stresses in the light irradiated layer and at the boundary between irradiated and non-irradiated parts of crystal. Investigation of the stress effects is actual because the stresses can initiate the processes of degradation and damage. On the other hand, the stresses can directly affect the polymerization processes. The investigations performed by optical and atomic force microscopy methods show, that the stresses can exceed the limit for fullerite damage. The damage processes are promoted by the reduction of dislocation mobility that causes the brittleness of fullerite. It has been shown that the relaxation of stresses occurs by generation and glide of dislocations, creep processes and crack formation. The crack formation in the fullerite polymer can been reduced by performing polymerization at elevated temperature (>320K). It is ensured by a lower level of stresses for the C_{120} phase as well as by the thermal activation of stress relaxation processes. It has been found that the applied load causes the creep and stress relaxation processes in fullerite crystals due to thermally activated movement of dislocations. The results confirm the relation $\sigma = B\,\acute{\varepsilon}^m$, where σ- is the applied stress, $\acute{\varepsilon}$ = dH/Hdt is the deformation rate (where H -is the hardness and t is the loading time) and m is the rate constant. The values m<0.1 where fond that characterize fullerite as a material with a low dependence of deformation rate on the applied stress, i.e. with a very low resource of the stress relaxation.

It has been observed that the increase of fullerite hardness follows after switching off the light reaching saturation after 2-3 days. This new effect of post-irradiation hardening increases with increasing the light exposure. The effect is explained by continuation of polymerization under residual stress.

The methodical results of the study confirm the advantages of the microindentation and dislocation mobility methods for investigation of the behaviour of photopolymerization in fullerite, essentially complementing the results obtained by other methods. These local methods allow us to investigate the light irradiation effects of crystal surface as well as their depth distribution that is impossible for commonly used spectroscopy and other integral methods. It has been established that typical structural states of fullerite show definite values of hardness. Therefore, the microhardness method can be used for the express recognition of different fullerite phases.

For the further investigations, it is of interest to perform more detailed studies of the photoinduced effects in a vacuum and different gaseous atmospheres, using dislocation mobility and microhardness methods. An actual task is the study of photopolymerization processes in thin fullerite films, which are preferable for practical applications.

The investigations are complicated because of a low light penetration depth in fullerite. The penetration depth for the red light is only few micrometers and in the region of ultraviolet light it becomes even less. As a result, the identification of different possible phototransformed phases with the commonly used methods is a difficult problem. This is a reason why in the present study we used mainly the structure sensitive microhardness and dislocation mobility methods exhibiting high spatial resolution. Their advantages are confirmed by previous studies.

Thesis

1. The conditions of photopolymerization are elucidated. It has been found that the photopolymerization is observed in the face-centered-cubic phase of fullerite in the temperature range of 260-400K under irradiation with UV and visible light irradiation in the fundamental absorption region at photon energies exceeding the threshold of 1,5-1.6eV, which correspond to photogeneration of excitons in fullerite. The photopolymerization occurs in the near-surface layer, which thickness corresponds to the light penetration depth in fullerite. The efficiency of polymerization increases with increasing the wavelength.
2. Two phototransformed phases, which differ in hardness and thermal stability, are found to appear: (a) well-known all-carbon polymer formed by fullerene dimers (C_{120}) and (b) the hard modification of the photopolymer (HV=0,65 -1 GPa). The hard photopolymer is formed in the subsurface layer of 0.5-1 μm at temperatures ranging from 290 to 340 K. This phase is thermally less stable and transforms to well-known fullerene photopolymer on heating at 310-320K.
3. The formation of two phases of fullerite photopolymer can be explained by the well known photochemical [2+2] reaction, in which depending on the conditions of experiment, all-carbon fullerene dimers (C_{120}) or $C_{120}O$ dimers

are created. In the later case, C_{60} molecules possibly are connected by an oxygen bridge and a single carbon bond.

4. It has been found, that the major role in the photopolymerization under irradiation with UV light at $\lambda \leq 150$ nm in air atmosphere that plays the photogeneration of ozone and its reaction with fullerite.
5. The effect of stresses created by photopolymerization has been investigated. It has been established that due to limited possibility of stress relaxation the degradation processes occur in fullerite photopolymer *via* formation of dislocations and crystallographically oriented system of microcracks. It has been found that the degradation processes can be reduced by performing polymerization at elevated temperature (>320K).
6. The effect of post-irradiation hardening has been observed., which manifests as an increase in hardness during the storage of light-irradiated fullerite crystals in dark. The effect is explained by continuation of the polymerization under residual stress.

Publications

The main results of the PhD study are published in 5 papers in International journals, reported on 3 International conferences.

The results are reported in 7 regional or local conferences and published in proceedings and abstract books.

Papers in International journals

1. I.Manika, J.Maniks, R.Pokulis, J.Kalnacs, D.Erts.Polymerization and Damage of C60 Single Crystals under Low Fluency Laser Irradiation. *Phys.stat.solidi (a)* vol.188, No.3, 989-998, 2001.
2. I.Manika, J.Maniks, R.Pokulis, J.Kalnacs. Effect of light exposure on dislocation mobility in fullerite C_{60} crystals. In In Optical Organic and Inorganic Materials, S.P.Ašmontas, J.Gradauskas, Editors, *Proceedings of SPIE* vol. 4415, p.284-289, 2001.
3. J.Maniks, I.Manika, J.Teteris, R.Pokulis. Indentation creep and stress relaxation in amorphous As-S-Se and As-S films. In: Optical Organic and Inorganic Materials, S.P.Ašmontas, J.Gradauskas, Editors, *Proceedings of SPIE* vol. 4415, p.44-47, 2001.
4. I.Manika, J.Maniks, R.Pokulis, J.Kalnacs. Illumination time-evolution and wavelength dependence of the photoinduced hardening of C_{60} crystals. *Fizika Tverdovo Tela*, vol.44,No.3,p.417-418, 2002.
5. I.Manika, J.Maniks, R.Pokulis, J.Kalnacs. Photoinduced Hardening and Reduction of Dislocation Mobility in C60 Single Crystals: The Wavelength Dependence. *Fullerenes, Nanotubes and Carbon Nanostructures* . 10(1),69-80,2002.

Reports on conferences

5th Biennial International Workshop “Fullerenes and Atomic Clusters (IWFAC’2001)”, St.Petersburg, Russia, 2-6 July, 2001.

1. I.Manika, J.Maniks, R.Pokulis, J.Kalnacs. Illumination time-evolution and wavelength dependence of the photoinduced hardening of C_{60} crystals. Abstracts, p.197.

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2. I.Manika, J. Maniks,J.Teteris, J.Kalnacs,R.Pokulis. Phototransformation and thermal oxidation of microcrystalline C_{60} films. Abstracts, p.54.

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3.J.Maniks, I.Manika, J.Teteris, R.Pokulis. Indentation creep and stress relaxation in amorphous As-S-Se and As-S films, Abstracts, p.34.

4. I.Manika, J.Maniks, R.Pokulis, J.Kalnacs. Effect of light exposure on dislocation mobility in fullerite C_{60} crystals, Abstracts, p.104.

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5. V.Paskevics, J. Maniks, J. Teteris, R.Pokulis. Relaxation of mechanical stresses in fullerene C60 and amorphous As_2S_3 films. Program, P.255-258.

17th Scientific Conference of Institute of Solid State Physics, University of Latvia, Riga, Latvia, 19-23 February, 2001

6. R.Pokulis, I.Manika, J.Maniks, J.Kalnacs. Wavelength dependence of the photopolymerization in fullerite C_{60} crystals studied by micromechanical methods. Abstracts, p.25.

16th Scientific Conference of Institute of Solid State Physics, University of Latvia, Riga, Latvia,14.-16February, 2000.

7. J.Maniks, I.Manika, J.Pokulis, J.Kalnacs. Relaxation of mechanical stresses in fullerite C60,
Abstracts, p.47.

Latvijas Fizikas biedrības 5.konference , Daugavpils, Latvija, 8.-11. Jūnijs 2000

8. R.Pokulis, I.Manika, J.Maniks, J.Kalnačs. Fotoinducēto mikrocietības un dislokāciju kustīguma izmaiņu spektrālā atkarība fullerīta C60 kristālos.

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9. V. Paškevičs, R. Pokulis. As-Se plāno kārtiņu biezuma nehomogenitātes ietekme.Tēzes, 37.lpp

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10.V. Pashkevich, R. Pokulis. Photoinduced changes in arsenic chalogenide films and fullerines.Konferences materiāli, pp 45-50.