Illumination time-evolution and wavelength dependence of the photo-induced hardening of C_{60} crystals

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The fullerite photopolymerization in air in the wavelength range 350–900 nm was investigated using microhardness and dislocation mobility methods. The photo-induced effects of hardening and reduction of dislocation mobility were found to increase linearly with increasing the photon energy. The existence of two phototransformed states is supposed from the kinetics data of photo-induced hardening.

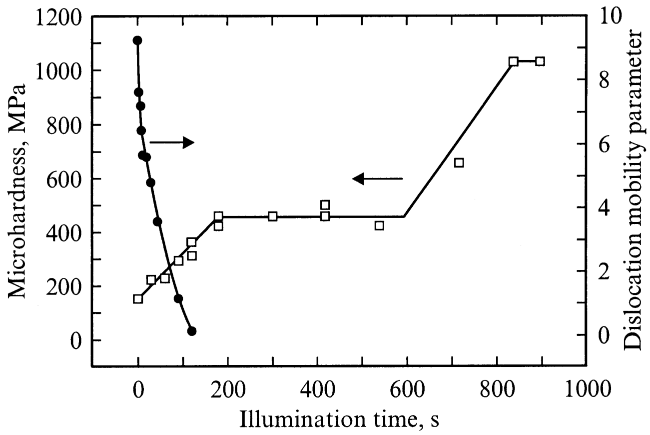
In the recent years the polymeric phases of fullerite C_{60} attracted much attention. The photo-induced polymerization of C_{60} is of special interest suggesting possible photolithographic and other applications of fullerite. Because C_{60} absorbs light very efficiently, the photopolymerization occurs in a thin near-surface layer thus the limited sample volumes available make a full characterization of phototransformed C_{60} rather difficult. According to the light absorption data, the thickness of the phototransformed layer depends on the wavelength. Formation of covalently bonded fullerene dimers or chains in the molecular lattice through photochemical $2+2$ cycloaddition reaction is considered as a main mechanism of photopolymerization [1]. Generally, an increase of the efficiency of photopolymerization with decreasing the wavelength was expected. However, investigations showed contradictory results. In [2], the photo-induced effect was found to appear under green light irradiation, but little or no effect was observed with red light, while in [3] a maximum of the effect was observed with red light. In the present study, the wavelength dependence and kinetics of the fullerite photopolymerization in air was investigated using microhardness and dislocation mobility methods.

1. Experimental details

C_{60} single-crystals were grown from the vapour phase in a temperature gradient by sublimation of a twice sublimed C_{60} powder (99.9% C_{60}). The density of "grown-in" dislocations was $10^3-10^4\,\mathrm{cm}^{-2}$. A typical approximate size of the samples selected for experiments was $0.5 \times 2 \times 7$ mm. Investigations were performed on the (111) face of as-grown crystals in the wavelength range of 350–900 nm at power density 2–140 mW/cm^2 and illumination time $1-5\cdot10^3$ s. The Vickers microhardness was measured at light loads (3.2–5.5 mN) to ensure the indentation depth lower or comparable with the thickness of the phototransformed surface layer. The microhardness tester with a vibration-insensitive loading system was used [4]. The scatter of the hardness measurements was typically about 12%, but for the smallest impressions it increased up to 22%. The dislocation structure around indents was obtained by selective etching the crystals in toluene. The parameters l/d or $\Delta l/l_0$ (where l_0 and l are the dislocation arm length before and after illumination, respestively, and Δl is the difference between them) were mainly used as the characteristics of phototransformation.

2. Results and discussion

An increase of the microhardness and decrease of the dislocation arm length in fullerite crystals under light-irradiation was observed, confirming earlier results [3,5–8]. The effects increased with decreasing the wevelength. A two-stage wavelength dependence of the photo-induced change in dislocation mobility was observed. For each stage, the magnitude of the effect linearly increased with increasing the photon energy. A higher slope was observed for photon energies 1.55–1.8 eV which are lower that the band gap and correspond to energies of exciton photogeneration in fullerite. Obviously, for incident photon energies above the bandgap (about 1.8–2 eV), the efficiency of excitation is lowered due to photogeneration of distant electron-hole pairs and their trapping at different lattice sites. The rate of phototransformation depends on the incident power density and light-irradiation time. Figure shows the kinetics of photo-induced change in hardness and dislocation mobility. The dislocation mobility gradually decreases with increasing the light exposure. It is supposed that photo-induced formation of fullerene dimers or chains is the main reason for the reduction of dislocation mobility. Some contribution is observed also from physically absorbed oxygen. Measurable change in the hardness was detected when the thickness of the phototransformed surface layer exceeded about $0.1-0.2\,\mu$m. The illumination time-evolution of the photo-induced hardening showed a stepwise behaviour. The saturation stage of hardening is ascribed to formation of well-known fullerite photopolymer phase with a definite concentration and spatial dictribution of the dimers and chains. This phase possess a constant hardness (450–470 MPa) and reverts to pristine



Dependence of the microhardness and dislocation mobility parameter (l/d) on the illumination time. Light-irradiation was performed with 632.8 nm wavelength at 147 mW/cm^2.

fullerite on heating in air above 470 K [5,6]. No photo-induced hardening is observed above 400 K [3]. An additional mechanism of the hardening was found to be involved at the saturation stage of phototransformation during which the harchess in a near-surface layer of $\sim 0.5\,\mu$m increased up to 0.6–1 GPa (Figure). This phototransformed state was thermally less stable. A photochemical transformation with participation of absorbed oxygen and creation of C–O–C linking bonds [2] or a higher extent of photopolymerization by formation of branched polymeric chains [9] could be responsible for the additional hardening. Moreover, the photopolymerization at the saturation stage could be affected by ctresses generated due to the difference in lattice constants of pristine and photopolymerized fullerite. Besides, the relaxation of stresses by generation of dislocations, stacking faults, displacement domains and cracks is observed which leads to substructure formation and hardening.

In conclusion, the results confirm an increase of the efficiency of photopolymerization with decreasing the wavelength. The existence of two phototransformed states is suggested from the kinetics of photo-induced hardening. The results show that the dislocation mobility method is useful for characterization of the initial stage, but the microindentation technique is applicable for investigation of the developed stage of phototransformation.

References

[1] P.C. Eklund, A.M. Rao, P. Zhou, Y. Wang, J.M. Holden. Thin Solid Films **257**, 185 (1995).

[2] M. Haluska, M. Zehetbauer, M. Hulman, H. Kuzmany. Mat. Sci. Forum **210–213**, 267 (1996).

[3] M. Tachibana, K. Kojima, H. Sakuma, T. Komatsu, T. Sunakawa. J. Appl. Phys. **84**, 1 (1998).

[4] G.P. Upit, S.A. Varchenya. In: Scientific Instruments / Ed. G. Matis. Zinatne, Riga (1986). P. 12 [in Russian].

[5] I. Manika, J. Maniks, J. Kalnacs. Latv. J. Phys. Techn. Sci. **3**, 12 (1997).

[6] I. Manika, J. Maniks, J. Kalnacs. Phil. Mag. Lett. **77**, 321 (1998).

[7] I. Manika, J. Maniks, J. Kalnacs. Fullerene Sci. Technol. **7**, 825 (1999).

[8] M. Tachibana, H. Sakuma, K. Kojima. J. Appl. Phys. **82**, 4253 (1997).

[9] T. Wagberg, P. Jacobsson, B. Sundqvist. Phys. Rev. **B60**, 4535 (1999).