Phase conjugation in amorphous selenium thin films

E. Haro-Poniatoowski, M. Fernandez-Guasti, and S. Camacho-Lopez

Universidad Autonomo Metropolitana Iztapalapa, Departamento de Fisica, Apartado Postal, 55-532, Mexico 09340 D.F., Mexico

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We report phase conjugation in amorphous selenium thin films with a 25-mW He-Ne laser. The phase-conjugate signal exhibits a maximum efficiency of 18%. Gratings were recorded with spatial frequencies of 275 lines/mm. We have performed micro Raman spectroscopy measurements between and on the lines that form the grating, and the results reveal the presence of amorphous selenium only. Scanning electron microscopy together with profilometry measurements indicate induced variations of the film thickness. However, this relief does not seem sufficient to explain the observed effects.

In the past few years a great deal of research has been done in studying amorphous chalcogenide films as a medium for optical storage. In particular, tellurium and selenium and their alloys have received special attention because of their excellent optical recording characteristics. Furthermore reversible optical memory effects have been reported in these systems. An important advantage of amorphous chalcogenide films over other materials is that they show relatively large nonlinearities at low incident powers. Phase conjugation (PC) in amorphous semiconductor-doped glasses has been extensively investigated. However, little information is available regarding purely amorphous semiconductor materials. PC has been reported in As₂S₃ (Ref. 5) and GeSe₂. The underlying mechanisms invoked to account for PC are electronic excitations and structural transformations.

In this Letter, we report on PC in amorphous selenium thin films using a 25-mW He–Ne laser (λ = 632.8 nm) through degenerate four-wave mixing. We study the PC efficiency as a function of the pump intensities as well as the temporal evolution of the signal. In the present conditions, a permanent grating is recorded in the selenium film. The behavior of the first-order transmitted diffracted beam is compared with that of the PC beam; these two signals, contrary to what is expected, show maximum efficiencies at different irradiation times.

In order to investigate the mechanisms involved in the generation of the PC signal, several techniques were used. Low-spatial-frequency diffraction gratings (275 lines/mm) were observed by means of an optical microscope with high contrast between fringes. Micro Raman spectroscopy measurements were performed in the bright and dark zones of the fringes. Raman spectra revealed the presence of amorphous selenium at both sites. Scanning electron microscopy and profilometry measurements were also carried out. The results indicate that the grating is formed by sublimation of selenium in the interfringes. However, the sublimation of selenium alone does not seem sufficient to explain the observed effects.

High-purity selenium was evaporated at a deposition rate of 0.4 nm/s onto Corning 7059 glass substrates. The thicknesses of the films were of the order of 4 μm. The samples were characterized by Raman spectroscopy.

The setup was placed on a stable holographic table because of the slow response time of the material, typically of the order of minutes. The experiments were done at room temperature in air. A 25-mW He–Ne laser beam (λ = 632.8 nm) was first expanded and focused. The focal length of the expander was adjusted to 1.80 m. The beam was split into two beams 0.09 m after the expander. The power densities obtained at the focal length for each beam were 2.27 W/mm² (pump beam) and 0.11 W/mm² (probe beam). Care was taken to ensure equal optical paths for both beams in order to have a high degree of mutual coherence. The angle of incidence between the two beams was set at 10 deg. The selenium film was positioned perpendicularly to the pump beam as shown in Fig. 1. Reflection on the film surfaces provided the counterpropagating pump beam necessary for PC through degenerate four-wave mixing. In the linear regime, the air–selenium interface yields a reflectivity of 22%, and the selenium–glass substrate interface yields a reflectivity of 7%. The linear absorption coefficient was estimated to be α = 3.45 × 10⁵ cm⁻¹, which yields a 75% absorption in the 4-μm film. The pump-beam reflectivity increased from 22% to 31% as the PC intensity increased to its maximum. This observation is the opposite of the specular diminishment observed by Pepper in BaTiO₃. Constructive interference in the Bragg planes generated by the counterpropagating pump beams may account for this increment at normal incidence. The intensity of the pump beam was varied from 0.38 to 2.27 W/mm². The PC signal was detected by means of a 4% beam splitter placed in the object beam at 0.3 m before it reached the sample. With this arrangement a grating with spatial frequency of 275 lines/mm was recorded. Four orders of diffracted beams were observed that correspond to the grating spatial frequency; similar ob-
The PC signal intensity together with the first-order diffracted intensity was plotted simultaneously against time (Fig. 3). The PC signal is approximately five times larger than the first-order diffracted signal. Both signals reach a maximum value before a decrease. This peaking behavior for the first-order diffraction has already been observed by Hou and Chang\(^8\) and by Song et al.\(^5\) in As\(_2\)S\(_3\) and Ge\(_2\)S\(_2\)C\(_{1-x}\), respectively. The former group claims that a saturation effect occurs and that the signal decays because of the destruction of the periodic nature of the phase grating owing to saturation, whereas the latter group invokes a crystallization effect that takes place at the fringes and after some time at the interfringes of the grating by heat diffusion, which causes a decrease in the first-order diffracted intensity signal. In our case these maxima do not coincide. The PC gratings were observed after an exposure time of several hours, which is well after the first-order diffraction grating signal decayed to a minimum, and no degradation of the grating was detected.

The theoretical model of degenerate four-wave mixing in a two-level atomic system, with absorption neglected, predicts that the transmitted probe beam and the PC signal achieve equal gain.\(^10\) Absorption has been taken into account for counterpropagating beams entering the sample from opposite sides; however, in our setup, the pump enters the sample from one side only, where no theo-

Fig. 1. Experimental arrangement used to generate and detect the PC signal.

Fig. 2. Temporal behavior of the PC signal for pump-beam intensities of 0.38 W/mm\(^2\) (curve a), 0.76 W/mm\(^2\) (curve b), and 2.27 W/mm\(^2\) (curve c).

bservations in Kerr-type media have been previously reported.\(^8\) In particular, the first-order diffracted beam emerges symmetrically displaced about the transmitted pump beam as shown in Fig. 1. The gain in this beam was found to be identical to the gain of the transmitted probe beam, and so that we could avoid the dc signal from the probe its gain was monitored through this first-order diffracted beam.

The PC intensity was plotted against time for different pump beam intensities (Fig. 2). The highest efficiency is obtained for a pump power density of 0.76 W/mm\(^2\) after 240 min. In all cases, the PC signal increases until it reaches a maximum value and then decreases. In most cases, the maximum efficiency peaks at shorter times as the pump power is increased. However, the reproducibility of the results is difficult. The film behaves in a highly nonlinear fashion, since twice the time exposure is not compensated by half the irradiation intensity. The maximum PC intensity is obtained for 0.76 W/mm\(^2\). The PC efficiency, defined as the quotient of the PC intensity over the probe intensity is 18\% at this maximum. The unevenness of the sample thickness greatly influences the phase-conjugated signal, yielding a 30\% PC reflectivity variation from point to point in the sample. We have observed that the PC signal increases logarithmically with the thickness of the film in the range of 0.1 to 4.0 \(\mu\)m.

Fig. 3. Temporal behavior of the PC signal and the first-order diffracted beam. Note that the maximum efficiency in the PC signal occurs after the maximum in the first-order diffracted signal.

Fig. 4. Optical microscope photograph of a 4-\(\mu\)m periodic grating in amorphous selenium.
retical models that include absorption have been made to our knowledge. Nonetheless, absorption alone seem unlikely to account for the observed effects.

In Fig. 4 we show a typical diffraction grating of 275 lines/mm obtained with pump- and probe-beam power densities of 2.27 and 0.11 W/mm², respectively. It was first supposed that the formation of the fringes could be due to an oxidation or a chemical reaction process. In order to discard possibilities we performed the same experiment but with the addition of a layer of glycerine in one case and with a layer of mineral oil in the other. The layers were deposited and covered with microslides. In both cases a well-defined diffraction grating was formed. Since the mineral oil and the glycerine are chemically stable, the possibility of sublimation of selenium in the interfringes is excluded.

A few years ago, PC in amorphous As₂S₃ thin films was reported. Those authors consider that the underlying mechanism involves band-gap transitions. In their case the irradiation energy was above the absorption edge of the material as opposed to the present case in which the excitation energy is below the absorption edge. Recently we reported PC in GeS₂₅ and we suggested that structural reorganization can occur at irradiation energies below the absorption edge. Previous studies indicate that amorphous selenium is composed by long rambling chains. Several types of bonding defects have been proposed, with some of them producing states below the absorption edge. Recently a comprehensive description of photostructural changes in chalcogenide glasses has been presented. According to these models photoinduced processes consist of two steps. At the first stages an electron–hole pair is created by the laser, and certain bonds are weakened. This leads to the displacement of the atom near the excited pair, which gives rise to the possibility that the recombination of the electron–hole pair takes place in a different atomic configuration. Thus it seems reasonable to assume that structural rearrangements caused by laser irradiation below the absorption edge can occur through the defects of the material.

Structural changes in the material can be detected by micro Raman spectroscopy. The size of the laser spot was approximately 2 µm, which is of the same order as the fringes. The intensity of the laser at 514.5 nm was 0.05 mW in order to prevent damage or crystallization of the film by the laser irradiation. The spectra obtained at the fringes and at the interfringes forming the grating were identical, and the spectra correspond to those of elemental selenium.

In Fig. 5 the transverse section of the grating obtained with a profilometer is shown. The periodicity of the grating is approximately 4 µm, and the groove depth is approximately 20 nm. These figures were confirmed by electron scanning microscopy. On the one hand, we have mentioned that the PC intensity increases with thickness, which suggests a volume effect rather than a surface one; on the other hand, the phase retardation introduced by the relief, i.e., the depth of the groove (20 nm) compared with the wavelength of the laser (632.8 nm) is 40/632.8, or =λ/10. This retardation may only produce low diffraction efficiencies, which suggests again that the surface relief is only partially responsible for the observed effect. Therefore some other process is taking place in the material. This process could be structural rearrangements involving the formation of ordered structures, these structures being too small to be detected by Raman spectroscopy.

In conclusion, we have reported PC in amorphous selenium with efficiencies of as much as 18%. The exposure time and the incident pump intensity behave in a highly nonlinear fashion, showing a well-defined maximum PC efficiency. One of the critical parameters for observing the PC signal is the thickness of the sample. The mechanism for the formation of the diffraction grating is sublimation of selenium combined with structural rearrangements.

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