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Reversible Laser-Induced Phase Transformation of Amorphous Selenium

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Abstract

Reversible changes in an optical density produced by a sharply forcused 6328A line of He-Ne lasr pulses have been observed in evaporated amorphous selenum films. Structural analises showed that the optical changes are related to the crystallization and the revitrification of the selenium films. These structural change take place in a spot of 1 to 5 μm in diameter. The phenomena were observed on the laser irradiation by the pulse durations of 10^{-3} to 10^{3} sec and the corresponding peak intensities of 1 to 10^{-2} mw. A model is developped in which both the speed of crystallization and the revitrification are attributed to the large enhancement of these rate under the influence of the photon flux.

§ 1. Introbuctlon

Multi-component amorphous semiconductors exhibit a memory effec as a current controll negative resistance[1]. It is rather well established that the memory effect is due to crystallization of the amorhous semiconductors by Joule heating[2]. Feinlib, deNeufville, Moss and Ovshinsky have reported that $Te_3Ge_5Sb_2S_2$ amo.phous semiconductor can be converted into a crytalline phase by exposure to a laser beam, instead of by Joule heating[3]. The present paper reports on the effects of irradiation of intense light beams on selenium films It was found that sharply forcused laser light induces reversible changes in optical properties of the films which are accompanied with phase transformations, from amorphous phase to crystalline one, or vice versa. Irradiation time-laser power characteristic showed the potential usefullness of amorphous films in erasable optical memory media.

§ 2. Experimental

Figure 1 shows a schematic illustration of sample structure. As shown in the figure, four-layered sandwich film composed of collosion-carbon-selenum-collosion (1500, 500, 800 ~1200 and 1500A in thickness, respectively) was formed on an electron microscope grid. Mettallic selenum with purity less than 0.001% was evaporated from a tantalum boat on a carbon coated collosion films held at room temperature under the condition of 5×10^{-5} Torr. The evaporation rate was about 1500 A/min and the thickness of the films were 800~1200 A.

Figure 2 shows an illumination setup used in this work. A 6328 A line of a pulsed He-Ne laser was forcused onto the amorphous selenum films by a 40 power objective of

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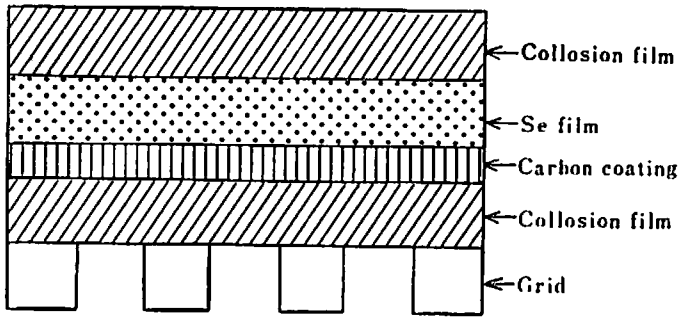

Fig. 1 Schematic illustration of sample structure.

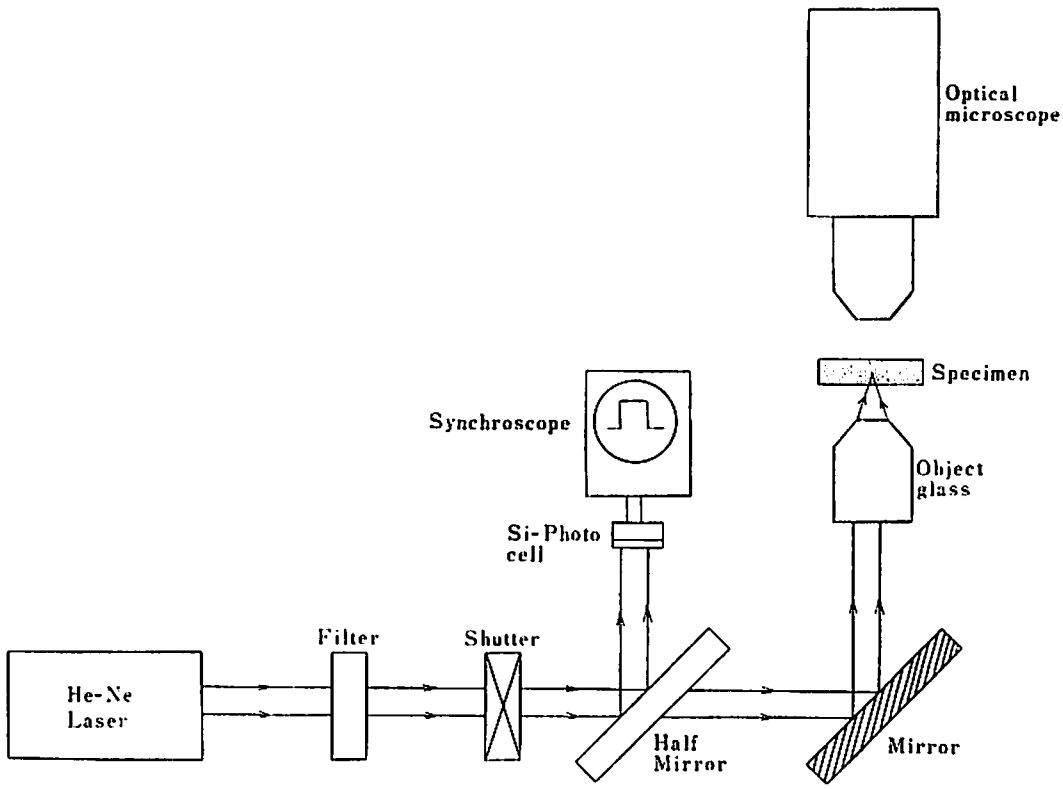

Fig. 2 Experimental setup for laser beam irradiation.

an optical microscope through the electron microscope grid. Power of the laser beam was controlled by the nutral density filters. A laser pulse was produced by a mechanical shutter and the irradiation time was monitored by a scynchrosope using a Si photodetector. Effects of the lasr beam irradiation on selenium films were examined by an 600 power optical microscope. After observing the effects of laser pulsing under an optical microscope, the samples were then placed, chalcogenide side up, on the cooling stage holder of an JEM-T7 (60 kv) electron microscope and were examined in transmission. A liquid-nitrogen stage helped keep the sample cool, and care was taken to avoid crystallization of the films in the electron beam.

§ 3. Results

The as-deposited films of selenium has dark red color which specifies the amorphous phase. The fiilms showed structureless electron microscopic image and gave rise to amor-

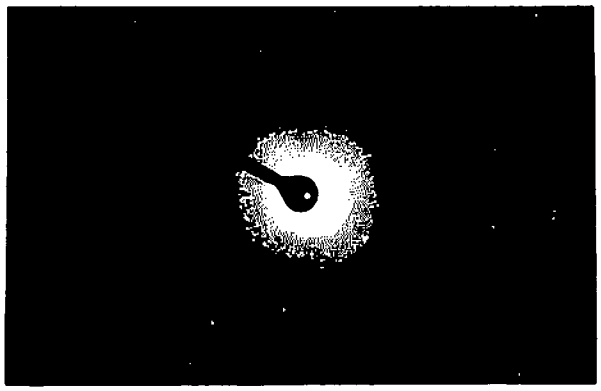

Fig. 3 An electron diffraction pattern of amorphous selenium film prepared by vacuum evaporation.

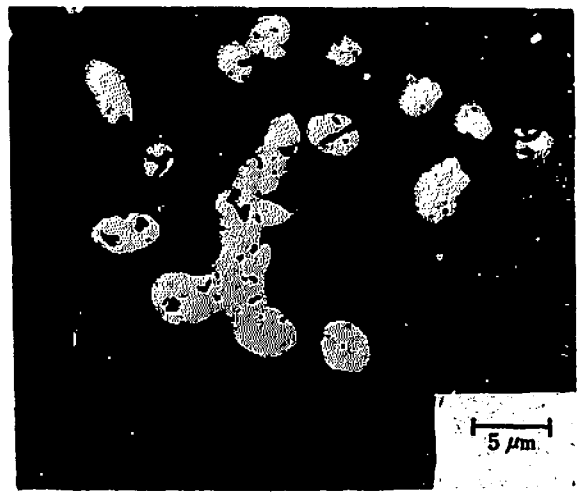

Fig. 4 An electron michroscope observation of slenium crystals.

phous patterns in electron diffraction as shown in Fig 3.

The amorphous films deposited on the carbon coated collosion films were rather stable compaired to those deposited on the glass substrate[4]. However, small selenium cryrtals, 1 to 5 μm in diameter, were observed in the amorphous films kept in dark for 3 to 4 weeks at room temperature.

Figure 4 shows an electron michroscope obsevation of the small selenium crystals. No growth of the selenium crystals was detected dring the electron michroscope obserbation[5]. Electren diffraction pattern of the selenium crystals showed a spotty-ring structure, indicating nearly single crystal as shown in Fig 5.

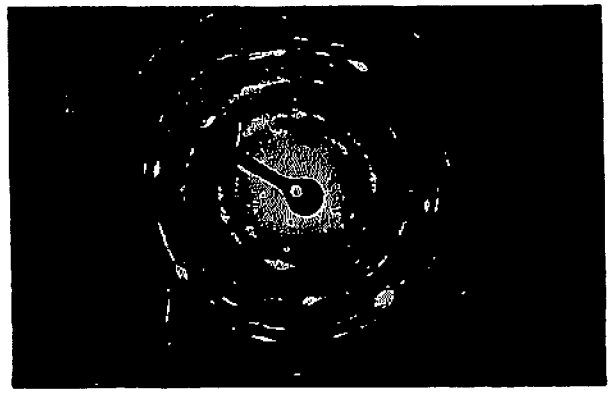

Fig. 5 An electron diffraction pattern from the selenium crystals grown at room temperature in the dark.

In the case of laser beam irradiation to the small selenium crystals, the optical transmission of the films decreases or increases according to the irradiation condition (heare after, decrease and increase of the optical transmission are respectively entitled "write" and "erase"). Typical result of the writting operation is shown in Fig 6.

As shown in the figure, diamter of the small selenium crytals increases after

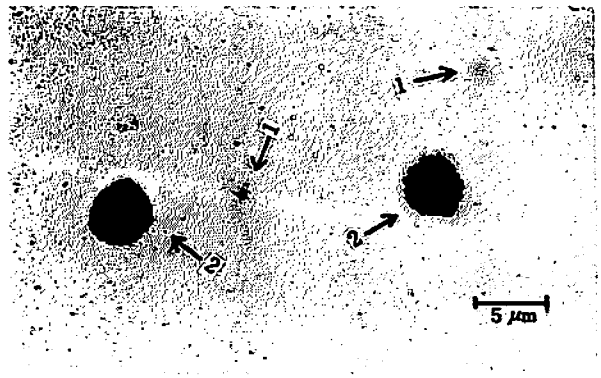

Fig. 6 Photomicrograph of written area. Number 1 indictaes the small selenium crystals befor laser beam irradiation and number 2 indicates laser beam irradiated selenium crystals. Irradiation time and laser power were 0.3 sec and 0.5 mW respectively.

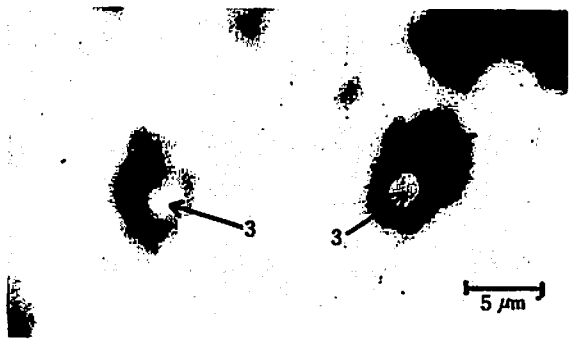

Fig. 7 Photomicrograph of erased areas. Erased ares (indicated by number 3) were obtained by laser beam irradiation with 0.8 mW in 1 msec.

laser beam irradiation. Electron microscope observation showed that the decrease of the optical transmission is related to the crystal growth of the selenium crystals. Figure 7 shows the photomicrograph of the erased areas.

As clearly seen in the figure, optical transmission of the erased areas are simillar to that of the amorphous area. Electron diffraction analises of the erased area showed the same hallow pattern as shown in Fig. 3, indicating that the erasing operation is related to the phase transformation from crystalline to amorphous state.

In order to get more informations for the writting and the erasing operations, relationships between these effects and irradiation conditions were studied in detail. Irradiation time-laser power characterestics of these effects are shon in Fig. 8.

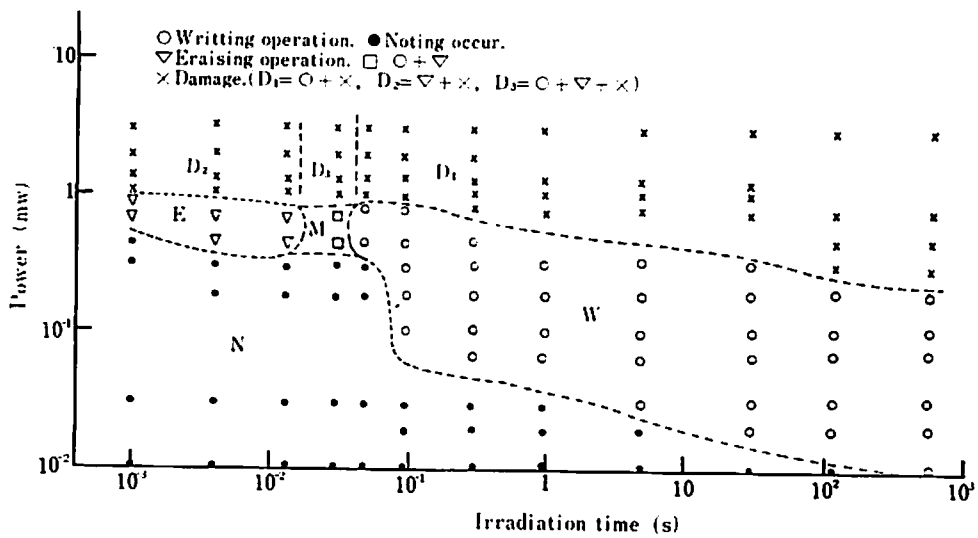

Fig. 8 Irradiation time-laser power characteristic of selenum films.

In the figure 8, writting and erasing operations are indicated by "*W*" and "*E*", respectively. In the *W* area, the diameter of selenium crystals increased proportional to the power of the laser light under the condition of constant irradiation time. However, strong light irradiation produced a empty hole in the center of the grown selenium crystals (indicated by D_1 in Fig. 8).

In the *E* area, the diamter of the erased region increased proportional to the power of laser light under the condition of constant irradiation time. However strong light irradiation made a empty hole in the center of the amorphized region (indicated by D_2 in Fig. 8). It was also possible to amorphize the grown selenium crystals in the *W* area. This indicate that the phenomenon is reversible. In the *M* area, the center of the irradiated region was amorphized and the round of the amorphized region was

crystalized. However intense irradialion produced a hole in the center of the amorphized region (indicated by D_3 in Fig 8). No effects of the larer beam irradiation were observed in the N area in Fig 8. Power density of laser beam necessary for the writting and the erasing operations were ranged 80 to 8×10^5 J cm^{-2} and 4 to 80 J cm^{-2} respectively.

§ 4. Discussion

In case of writting opecation, maximum crysal grouth rate was estimated about 2×10^5 μm hr^{-1}. This value is about three order of magnitude larger than that for the case of pure thermal process reported by Kawarada and Nirhina[6]. This suggest that the ovserved csystal growth is infuluenced not only by thermal process but also by the creation of excess electron-hole carriers as reported by Dresner and Stringfellow[7].

It is speculated that the dynamical amorphization observed in this study cannot be associated wuith a crystalline to liquid transformation. This is confirmed by the fact that the collosion films adjacent to selenum films were not damaged at all. This fact indicates that the temperature of the samples did not go up so high as the melting point of the collesion films (~170°C) which is far lower than that of crystalline selenium (220°C). This amorphization process is consistent with the electron beam induced one reported by Herd and Cnaudhari[8] from the phenomenological point of view.

§ 5. Conclusion

Effects of the irradiation of 6328 A line of He-Ne laser beam on the evaporated amorphous selenium films were investigated. It is found that the decrease of the optical trasmission is related to the phase change from amorphous to crystalline state and the increase of the optical transmission is related to the phase change from crystalline to amorhous state.

Reversible optical changes accompanied with phase transformations were observed for various pulse duration of 10^{-3} to 10^3 sec and corresponding peak intensities of 1 to 10^{-2} mW in a spot of about 3μm in diameter.

Oveservation of these photo-induced rapid reversible phase transformation suggests the existence of excess-carrier-assisted-rearrangement of local structural nature of selenium.

Aknowlegement

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