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A PHOTO-INDUCED MEMORY EFFECT OBSERVED ON In-Si-Se SYSTEM

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Abstract: A photo-induced memory effect (a phenomenon similar to the persistent photoconductivity) was found in the photo-induced polycrystalline films of the In-Si-Se system. The photo-induced polycrystalline process was performed by irradiating the specimen (the light intensity is 6 mW/cm²) at temperature 70°C. The conductivity drastically increased by irradiation of the light pulse (its intensity is 20 μW/cm²) at low temperature (153 K) and entered a memory state. With increasing the temperature above a critical point (T=263 K), the conductivity returned to the original value. As the photo-induced memory effect is a reproducible phenomenon, it may be considered as an electronic effect and seems to be explained by the barrier model with various inhomogeneities in the polycrystalline films.

1. Introduction.- A photo-induced memory effect of annealed films under illumination is described for the In-Si-Se system[1]. The Arrhenius' plot of conductivity of the film annealed under illumination results in a nearly straight line at the cooling process and its activation energy is 0.4 eV. The moment the specimen was irradiated by a light pulse (its intensity is 20 μW/cm²), the conductivity changed drastically from $3 \times 10^{-10} \text{(ohm-cm)}^{-1}$ to $6.3 \times 10^{-6} \text{(ohm-cm)}^{-1}$. This low resistivity is a stationary state, that is, a memory state because the value of the conductivity does not change although the temperature increases from T=153 K to T=263 K. As the photo-induced memory effect is a reproducible phenomenon, it may be taken as an electronic effect.

Several physical models for the photo-induced memory effect have been proposed recently[2]. First, the persistent photoconductivity is observed in Te-doped $\text{Al}_x\text{Ga}_{1-x}$As crystal[3]. The dominant features of this type are; (a) apparently enormous Stokes shift, and (b) a very small thermally activated electron-capture cross section for temperatures below about 77 K. These features could be semi-quantitatively explained by a somewhat unorthodox configuration coordinate model.
Second, the barrier model which is induced by the inhomogeneities of the microcrystalline semiconductors is reported\(^4\).

For the photo-induced memory effect observed in the In-Si-Se system, the barrier model associated with various inhomogeneities will be accepted and we will further examine it.

2. Experimental.- In, Si and Se elements of different atomic percents were first melted in evacuated quartz ampoules at 1100°C for 10 hours. The ampoules were then quickly quenched to the room temperature. The film specimens were prepared by evaporating, for example, the melt-quenched In\(_2\)Si\(_{0.1}\)Se\(_{0.9}\)\(_{1-z}\) onto the glass substrate. Its temperature was about 30°C, followed by another deposition of an upper metallic comb-type Au electrode. The deposition rate was 50 Å/sec and the pressure was 2x10\(^{-5}\) Torr. The thickness of the film was about 0.5 to 1.0 μm. The annealing process was performed by irradiating the specimen on a heated plate with an incandescent lamp through an IR absorption filter (its intensity is 6 mW/cm\(^2\)). The annealing temperature for the Si rich samples was 70°C and that for the In rich ones was 100°C. When the "as deposited" film was heated in darkness, the nucleation for crystallization was formed at the interface between the substrate and the film. The speed of crystallization was very slow. But, under illumination, the nucleation generated at the interface rapidly reached the free surface side as a result of fast growth. Following this, the spectral response of the photocurrent in the In\(_{0.1}\)Si\(_{0.1}\)Se\(_{0.9}\)\(_{0.9}\) film before and after the annealing process (for 15 minutes) was measured. The shift of the peak value from 2.68 eV to 2.03 eV was clearly observed\(^5\).

3. Results.- It is shown in Fig.1 that the value of the optical gap \(E_{\text{opt}}\) taken from the intercepts of the \((\alpha h\nu)^{1/2}\) vs \(h\nu\) curves extrapolated to \(\alpha =0\), decreases towards lower photon energy with increasing illumination time; where \(\alpha\) is the absorption coefficient (\(E_{\text{opt}}\) value of 1.92 eV, 1.80 eV and 1.65 eV were obtained by illumina-
onto the glass substrate varied with the annealing process. This variation was examined using X-ray diffraction. From Fig.2(a) and (b), the occurrence of crystallized peaks was recognized in the In$_{0.1}$(Si$_{0.1}$Se$_{0.9}$)$_{0.9}$ film annealed for 15 minutes. No identification of the crystalline Se and the crystalline Si was obtained. However, it is considered from a comparison of Fig.2(b) with (c) that some of the crystallization effect related to the Si-Se system is certainly induced by the annealing process.

It is shown in Fig.3 that the Arhenius' plot of conductivity of the film annealed for 15 minutes results in a nearly straight line in the cooling process from point A to point B (the activation energy is 0.4 eV). The moment the specimen was irradiated by a light pulse (its intensity is 20 µW/cm$^2$) at point B in Fig.3, the conductivity changed drastically from point B to point C and then gradually settled down to point D with a decay time of few minutes. Point D is a stationary state, that is, a memory state because the value of the conductivity does not change although the temperature increases from point D to point E. With increasing temperature above point E, the conductivity returned to the original value.

Figure 4 shows the transient response of the photo-induced memory effect at $T=153$ K. It is clear that the transient response is affected remarkably by the wavelength of illumination, and for the short wavelength of light ($\lambda=6000$ Å; $h\nu=2.07$ eV), the transient response is rapidly changed. The transit time from low conductivity to the high one is about 1 msec. Also, it is interesting that the conductivity of photo-induced state illuminated by $\lambda=6000$ Å increases as compared with that illuminated by $\lambda=8000$ Å.
The conductivity ratio before and after illumination by a light pulse (at $T=183$ K) for the samples with different components are shown in Fig. 5. It is interesting that the samples of $\text{In}_0.1(\text{Si}_{0.1}\text{Se}_{0.9})_9.9$ and $\text{In}_{0.2}(\text{Si}_{0.1}\text{Se}_{0.9})_{0.8}$ show the largest value for the conductivity ratio in the In-Si-Se system.

4. Discussion.
As mentioned above, the photo-induced crystallization (the annealing process with light illumination) is necessary for the memory effect, because the inhomogeneities due to photo-crystallization play an important role.

In order to clarify the mechanism of the annealing process, the photo-induced crystallization was observed at the various stage of the annealing process under the illumination or in darkness by the optical microscope. It was recognized from these results that the crystallization rate induced by illumination was greater than that for heating in darkness.

Figure 6 shows the crystallization process under the illumination for the amorphous $\text{In}_0.1(\text{Si}_{0.1}\text{Se}_{0.9})_9.9$ film. It has been clear that the nucleation for photo-induced crystallization is smaller and the number of the nucleation is much larger than that in darkness.

A qualitative explanation for these results would appear to derive from the special characteristics of the defects, which is described in terms of the valence alternation pairs by Kastner[6]. The positively charged threefold-coordinated $C_3^+$ and the negatively charged, singly-coordinated $C_1^-$ atoms occur in pairs in the chalcogenide semiconductor.

We shall first consider the case of the amorphous Se to understand the process of the photo-crystallization. Under the illumination, the reaction
may be considered. In due course, the equilibrium between the direct and the reverse processes defining the new structural state of the material is established. We may suggest that the photo-crystallization proceeds when the direct process is dominant in the reaction (1). An admixture of the fourfold Si and the threefold In atom to the two-fold Se atom leads to the more complex structure. Thus, it must be considered that these atoms are involved in the process described by the reaction (1), because the Si-Se bonds play a dominant role in the photo-crystallization process in the In-Si-Se system.

There have been many papers of the photo-induced memory effect in the various semiconductor materials. However, it is accepted in the In-Si-Se system that the observed memory effect is due to the presence of macroscopic potential barriers associated with various polycrystalline inhomogeneities.

Figure 7 shows the schematic representation of the macroscopic potential barrier. In this model, we shall assume that the conductivity is governed by the current flowing across the effective barrier of some typical interface, located at \( z=0 \). Here, \( \varphi_{sd} \) and \( \varphi_s \) are the heights of the equilibrium and nonequilibrium drift barriers, respectively. \( E_C \) and \( E_V \) are the conduction and valence band edge.

According to the barrier model, the ratio of the current across the drift barriers in the residual conductivity state (\( I_r \)) to the current in darkness (\( I_d \)) is

\[
\frac{I_r}{I_d} \sim \exp\left(\frac{\varphi_{sd}}{kT}\right).
\]

When \( \varphi_{sd} \gg kT = 0.013 \) eV (at \( T=153 \) K), the current ratio \( I_r/I_d \) is very large and the conductivity change observed in Fig.3 seems to be well understood.

For the photo-induced memory effect in the In-Si-Se system, it is clear that the enhancement of the inhomogeneities due to the photo-crystallization and the increase of the barrier height in darkness are necessary for the photo-induced memory effect.

In summary, a photo-induced memory effect is found in the microcrystalline films of the In-Si-Se system. The conductivity ratio of \( \sigma_r/\sigma_d = 2.1 \times 10^8 \) is obtained at \( T=153 \) K. As this memory effect is a reproducible phenomenon, it may be considered as an electronic effect. The observed memory effect will be explained by the barrier model associated with various polycrystalline inhomogeneities.

References
