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The Influence of Moisture on the Storage Phenomenon in As_2Se_3 Evaporated Films

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The influence of moisture on the persistence of photoconduction has been investigated on sandwich type cells with an evaporated As_2Se_3 film and two evaporated Al electrodes. While the phenomenon is observed in the cells prepared by moisture-free processes, no storage is observed in the cells with theelectrodes containing adsorbed water. Thus water is shown to plays an important role in the disappearance of the storage phenomenon.

§ 1. Introduction

Some investigations have been reported on the photoconductivity of evaporated films of As_2Se_3,[1] and it was suggested that these films might be available for photoelectric targets of vidicon.[2] The films of As_2Se_3 evaporated in vacuum are amorphous and show hole conduction. The photoelectric characteristics of the films depend upon the material of the electrode with a positive voltage. When the positive electrode is of NESA coating, a storage phenomenon is observed.[3,4]

The storage phenomenon is that a current larger than the dark current continues to flow after taking off illumination. If the applied voltage is removed when this storage current is flowing, a current nearly equal to the original dark current flows by re-application of the voltage.

In the work of Turnbull,[3] no storage phenomenon was observed when Al was used for the positive electrode and it was suggested that the storage phenomenon was attributed to the trapping effect in the bulk layer. In the work of Yoshida,[4] even though Al was used for the positive electrode the storage phenomenon was observed when the electrode was not exposed to air. It was proposed that the storage phenomenon was attributed to the change of the barrier from blocking action to injecting action under illumination and a strong electric field and that the disappearance of the storage phenomenon was due to the oxide layer when the electrode was exposed to air.

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In the present experiment, the storage phenomenon was observed in the cells prepared by moisture-free processes when Al was used for the positive electrode. However, no storage phenomenon was observed when the Al electrode was held in wet atmosphere. Furthermore, the storage phenomenon was observed, even though an insulating layer was built in between Al electrode and As_2Se_3 layer, provided that the substrate was not held in wet atmosphere before evaporation of an As_2Se_3 film. This paper describes effects of moisture and insulating layer on the storage phenomenon in connection with the preparation of cells.

§ 2. Preparation of Cells and Measurements

As_2Se_3 powder used was prepared as follows. A mixture of high purity elements, As (99.9999%) and Se (99.999%), was weighed so as to have a stoichiometric constituent of As_2Se_3. This mixture was sealed in a quartz tube evacuated to 10^{-5} Torr. The quartz tube was heated up to 750°C for 10 hours, and it was gradually cooled down to room temperature. An experimental cell was of a sandwich type as shown in Fig. 1. A glass-

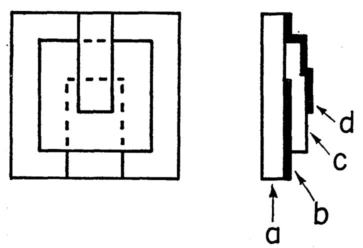

Fig. 1. Schematic illustration of the cell: (a) glass substrate, (b) glass-side electrode, (c) As_2Se_3 layer, (d) surface-side electrode.

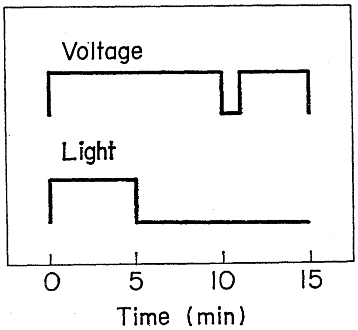

Fig. 2. Measurements of response characteristics.

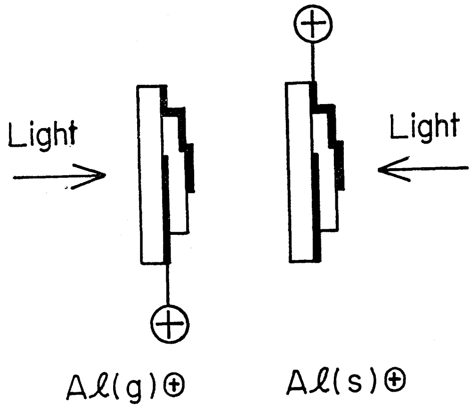

Fig. 3. Arrangements of polarity of an applied voltage and a direction of an incident light.

side electrode, an As_2Se_3 layer and a surface-side electrode were evaporated in a vacuum of 10^{-5} Torr. The thickness of As_2Se_3 films was 0.9 microns and it was controlled by weighing As_2Se_3 powder to be evaporated. The effective area of electrodes was 5×5 mm^2.

The photoelectric characteristics were measured by the procedure as shown in Fig. 2. Voltage and illumination were applied to the cell at $t=0$ min, and the illumination was taken off at $t=5$ min. The voltage was once removed at $t=10$ min and again applied to the cell at $t=11$ min in the dark. The illumination was introduced through the positive electrode. Monochromatic light was obtained with a Shimadzu IV-50A spectrophotometer at the exit slit width of 2.0 mm. All of measurements were carried out in vacuum. When the glass-side electrode or the surface-side electrode was positive, this arrangement was denoted by Al(g)⊕ or Al(s)⊕, respectively, as shown in Fig. 3.

§ 3. Experimental Results

3.1. *The influence of moisture on the Al(g)⊕ response characteristics*

No storage phenomenon was observed and the dark current was small in the cell made by such process that the glass-side electrode was exposed to air prior to evaporation of As_2Se_3. This was in accord with the results obtained by Turnbull[3] and Yoshida.[4] However, a remarkable storage phenomenon was observed in the cell prepared by such process that As_2Se_3 was evaporated onto the glass-side electrode degassed by heating at about 300°C in vacuum.

The following experiments were conducted in order to investigate these phenomena in detail. After the glass-side electrode was deposited on a glass substrate, it was kept in dry or wet oxygen (or argon) of 0.65 atm. pressure for one day. It was then re-evacuated. By using such methods, cells of types (a), (b), (c) and (d) were prepared. Fig. 4 shows the Al(g)⊕ response characteristics of them. The applied voltage was 5.0 V and the wavelength of an incident light

Table 1. Preparation Process of Cells (○: performed process).

Process / Cell	Evaporation of Al(g)	Oxidation in Oxygen	Evaporation of SiO	Holding in Atmosphere: Oxygen		Holding in Atmosphere: Argon		Evaporation of As_2Se_3	Evaporation of Al(s)
				Dry	Wet	Dry	Wet		
Type (a)	○			○				○	○
Type (b)	○				○			○	○
Type (c)	○					○		○	○
Type (d)	○						○	○	○
Type (e)	○	○						○	○
Type (f)	○		○					○	○
Type (g)	○		○				○	○	○

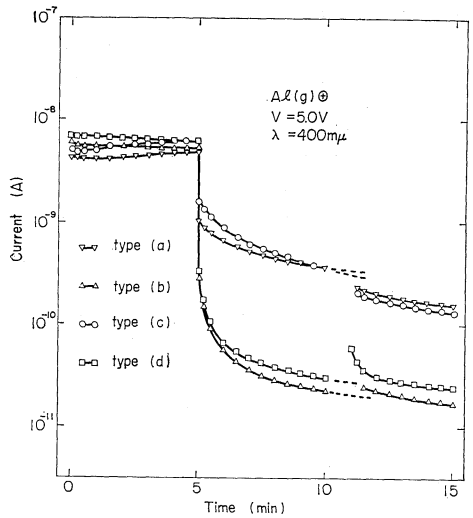

Fig. 4. The influence of atmosphere on the Al(g)⊕ response characteristics of types (a), (b), (c) and (d). They are exposed to dry oxygen, wet oxygen, dry argon and wet argon before evaporation of As_2Se_3, respectively.

was 400 mμ. While the storage phenomena were observed in types (a) and (c) which were exposed to dry oxygen and dry argon, respectively, no storage phenomenon was observed and the dark current was small in types (b) and (d) which were exposed to wet oxygen and wet argon, respectively.

Yoshida[4] has reported that the disappearance of the storage phenomenon was due to the insulating oxide layer formed on the surface of Al electrode. In the present experiment, however, water adhering to the surface of Al electrode seemed to have the effect of diminishing the storage phenomenon and the storage phenomenon was observed when the water was removed by degassing.

3·2. *The influence of moisture on the Al(s)⊕ response characteristics*

The large dark current and the storage phenomenon were observed in the Al(s)⊕ response characteristics when they were measured immediately after the preparation in all cases. This was in accord with the results obtained by Yoshida.[4] When these cells were kept in the moisture-free atmosphere such as vacuum or dry oxygen, the dark current was invariable and the storage phenomenon was still observed. On the other hand, when the cells were kept in wet atmosphere the dark current decreased and no storage phenomenon was observed.

It was reported by Yoshida[4] that the storage phenomenon disappeared when the cell was exposed to air and that this was because a thin insulating layer of oxide was formed at the boundary between As_2Se_3 and the surface-side electrode. In the present experiment, however, the storage phenomenon disappeared when the cell was kept in wet atmosphere. It seems that water plays a more important role than oxygen in the disappearance of the storage phenomenon.

3.3. *Insertion of an insulating layer*

The cells with an insulating layer between the glass-side electrode and As_2Se_3 layer were prepared to investigate the influence of the insulating layer and moisture on the storage phenomenon. This insulating layer is Al_2O_3 layer formed by heat-treatment of the Al electrode in dry oxygen, or SiO layer deposited. Type (e) has an Al_2O_3 insulating layer and type (f) has a SiO insulating layer. They were prepared by moisture-free processes. The Al_2O_3 layer and the SiO layer were about 0.01 microns thick and 0.03 microns thick, respectively. While type (g) had the same construction as type (f), it differed from type (f) in that the glass-side electrode and SiO insulating layer were kept in wet argon prior to evaporation of As_2Se_3.

As clearly shown in Fig. 5, the storage phenomena were observed in types (e) and

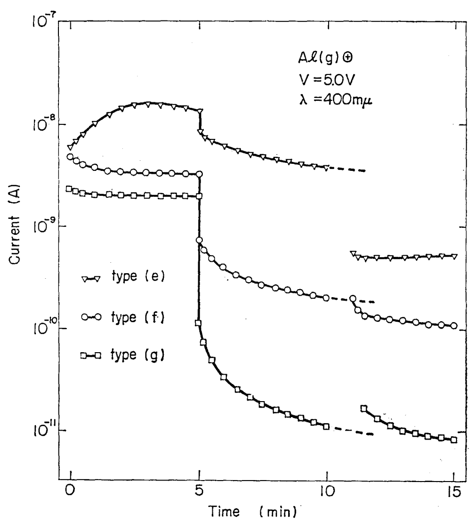

Fig. 5. The influence of insertion of an insulating layer on the Al(g)⊕ response characteristics of types (e), (f) and (g): (e) insertion of Al_2O_3 layer, (f) insertion of SiO layer, (g) insertion of SiO layer kept in wet argon.

(f) in spite of the existence of the insulating layer. However, no storage phenomenon was observed in type (g). Therefore, the insulating layer did not always cause the disappearance of the storage phenomenon.

§ 4. Discussion and Conclusions

In the present experiment, the influence of moisture and insulating layer on the storage phenomenon have been investigated. The storage phenomenon was observed in the cells prepared by moisture-free processes but not observed in the cells with Al electrodes containing adsorbed water regardless of whether an insulating layer was built in or not.

It was reported by Turnbull[3] and Yoshida[4] that the As_2Se_3 layer had the storage phenomenon when a NESA coating was used as a positive electrode. Yoshida gave an energy diagram for the contact between NESA coating and As_2Se_3 as shown in Fig. 6(a) The resistance of the As_2Se_3 layer decreases under illumination and thus the greater part of the voltage is applied to the barrier. As a result, the field-excitation of electrons and tunneling of holes are made possible by the electric field in the barrier and the energy band structure is given as shown by broken lines in Fig. 7. This hole tunneling continues and the large current flows so long as the voltage is applied even if the illumination is taken off. When the applied voltage is removed, the field-excited electrons return to the filled band and the hole injection is brought to a stop and then the current nearly equal to the original dark current flows and the energy band structure is given as shown by full lines in Fig. 7. Furthermore, Yoshida described that when the cell was exposed to air the storage phenomenon disappeared because the voltage drop in the insulating oxide layer on the surface of Al electrode made the field intensity in the barrier too small to excite electrons as shown in Fig. 6(b).

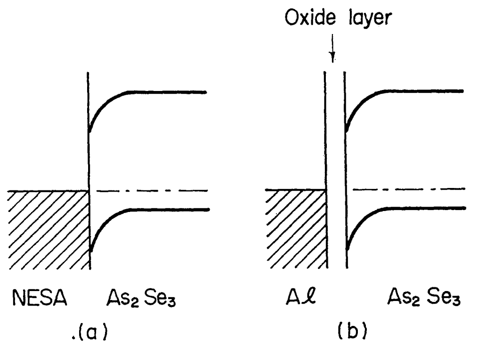

Fig. 6. Energy diagrams of (a) NESA-As_2Se_3 system and (b) Al-Al_2O_3-As_2Se_3 system. (After Yoshida.[4])

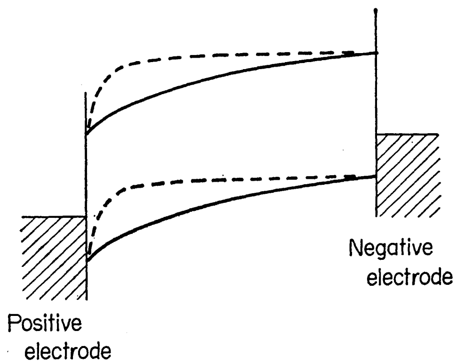

Fig. 7. Energy diagram of NESA-As_2Se_3 system for explanation of storage phenomenon. (After Yoshida.[3])

In the present experiment, however, the storage phenomenon was observed in the cells prepared by moisture-free processes. It disappeared when the Al electrode was kept in wet atmosphere. Furthermore, the existence of Al_2O_3 or SiO insulating layer did not always cause the disappearance of the storage phenomenon.

Some mechanisms may be considered to explain the present results. The first is that the adsorbed water, acting as a kind of catalyst, increases the rate of formation of oxide layer on the Al electrode. The second is that an insulating hydroxide layer is formed on the surface of Al electrode by the adsorbed water. These insulating layers make the field intensity in the barrier too small to excite electrons and thus no storage phenomenon is observed. The third is that the form of the barrier layer is influenced by the

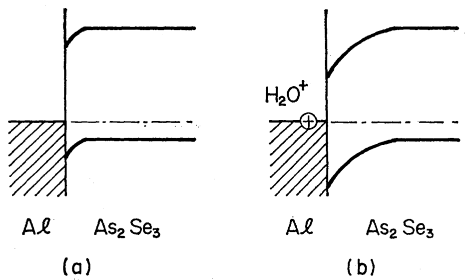

Fig. 8. Energy diagrams of Al-As_2Se_3 system (a) without H_2O adsorbed and (b) with H_2O adsorbed.

adsorbed water. That is, the energy band structure without adsorbed water is given as shown in Fig. 8(a). Since the barrier is low and narrow, the field-excitation of electrons is possible and the hole injection is caused. Thus the storage phenomenon is observed. When there are water molecules between Al electrode and As_2Se_3 layer, they give electrons to As_2Se_3 and change the enegy band structure as shown in Fig. 8(b).[5] Since the barrier is high and broad in this case, the field intensity in the barrier is impossible to excite electrons and thus no storage phenomenon is observed. The experimental results obtained by inserting an insulating layer suggest that the third mechanism seems to be most probable.

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