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Photovoltaic Effect of Germanium Thin Film Obliquely Deposited in Vacuum

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Abstract

A germanium film prepared by vacuum evaporation and deposited at an oblique angle of incidence on a glass substrate exhibits a very large photovoltaic effect. The magnitude of photovoltage reaches as high as 330 V for a film of 0.6 mm long (5,500 V/cm) under appropriate condition. For this effect to appear, it is necessary that the evaporation and deposition of germanium is made obliquely and that oxygen is adsorbed on the germanium film thus formed. When the deposition is made obliquely, fine crystallites grow in the direction of the evaporator from the numerous crystal nuclei formed on the substrate in the beginning. Thus, a thin film is composed in which fine crystallites arrange themselves with a definite orientation. When the film is illuminated by light, minute photovoltage is generated in every one of the crystallites and the sum of these voltages along the length of film becomes a high voltage between both ends of the film.

1. Introduction

It was shown by Goldstein and Pensak[1] that a film of cadmium telluride, prepared by vacuum evaporation and deposited at an oblique angle of incidence onto a heated substrate of glass or sapphire, exhibited a very large photovoltaic effect. The authors[2,3] and Kallmann et al.[4] also found that a film of germanium or silicon exhibits a similar phenomenon. Studies on this phenomenon and considerations on the generation of photovoltage will be reported below.

An example of the results is shown in **Table 1.** The measurements were made on a sample with film length 0.6 mm. The photovoltage is proportional to the length of the film as will be described below. From this proportionality, the values for a unit film length (1 cm) are reduced and given in the table. It is significant that the magnitude of the photovoltage increases when the film is left in vacuum or cooled to a low temperature. These values are several orders of magnitude larger than those which can be expected from a P-N junction of germanium.

Table 1 Measured photovoltage.

Condition		Photovoltage	
	Temperature	Measured	Per unit film length (1 cm)
In air	At room temp.	2.2 V	37 V
In vacuum	At room temp.	7.5 V	130 V
	Cooled by liquid air	330 V	5,500 V

Deposition angle: 60°
Film length: 0.6 mm
Light intensity: nearly that of sun light

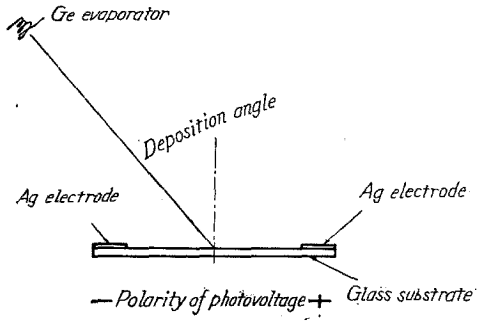


Fig. 1 Schematic arrangement for deposition.

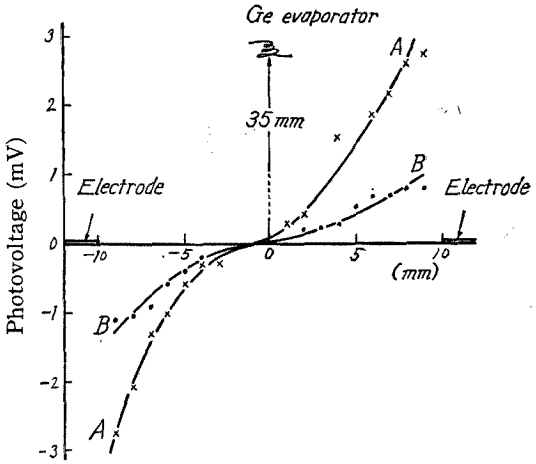
2. Experimental Procedure

The evaporation of germanium was carried out in an evacuated bell chamber. A glass sheet was employed for the substrate on which silver was deposited at both ends by vacuum evaporation as electrodes. Germanium was deposited at an oblique angle of incidence from the evaporator as shown in **Fig. 1.** Vacuum was maintained at about 1×10^{-5} mm Hg during the evaporation and deposition. The rate of deposition was approximately 100 Å/min. After the deposition, the film was taken out of the vacuum chamber and the measurements of photoelectrical properties were carried out with the light from an incandecent lamp through an infrared absorbing filter. The photovoltages were measured by using a vibrating reed electrometer with an external biasing d-c circuit.

3. Necessary Conditions for Photovoltaic Effect to Appear and Considerations on the Effect

3.1 Oblique Deposition

For the germanium film to exhibit a high photovoltaic effect, the deposition should be made at an oblique angle of incidence. The deposition angle is defined as that between the direction of deposition and the direction



Width of light beam = 1 mm
Film thickness (at the center)
A 820 Å *B* 1340 Å

Fig. 2 Photovoltage *vs.* position of the illuminating light.

perpendicular to the substrate. In **Fig. 2,** germanium was evaporated from the evaporator held above the center between electrodes. A narrow beam of light, 1 mm wide, was moved in the direction parallel to the length of film, and the photovoltage between electrodes was measured. As is shown in **Fig. 2,** no appreciable photovoltage appears directly beneath the evaporator. But the photovoltage is found to increase with the distance from the center and its polarity to become opposite on both side. This phenomenon shows that the oblique deposition is a necessary condition for the photovoltaic effect to appear with the positive voltage on the side opposite to the evaporator.

To obtain the relation between the deposition angle and the photovoltage, measurement should be made on films of the same thickness, hence the following method was adopted. Three substrates were held at different distances from evaporator and the deposition of germanium was made on them at the same time. The deposition was controlled by timely shielding to obtain equal thickness of film on all the substrates as shown in **Fig. 3.**

The photovoltages were measured in air with a narrow beam of light, 1 mm wide. The relations between the location of the incident light and the photovoltage are shown also in **Fig. 3.** When the photovoltages thus obtained on films of the same thickness are compared with one another, the photovoltage

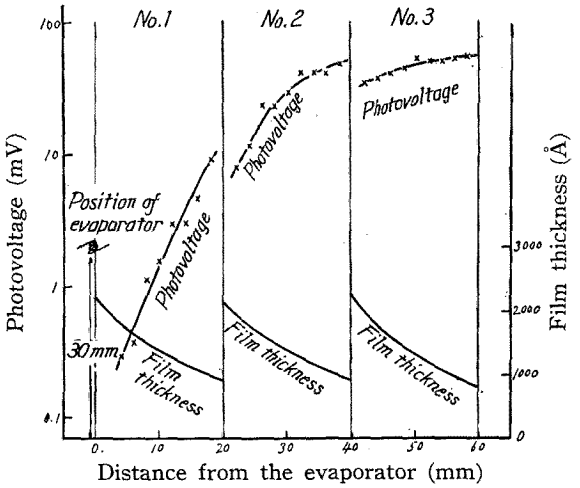


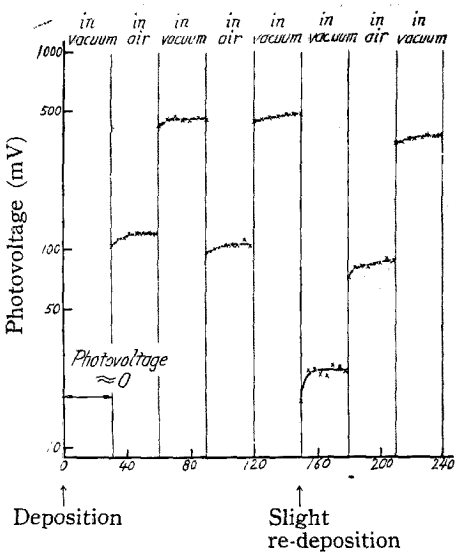
Fig. 3 Photovoltage *vs.* deposition angle. The photovoltages are measured by illuminating the film with a narrow light beam of 1 mm wide. It increases with the deposition angle, however, almost stops increasing above 60° of the deposition angle.

is clearly seen increasing with the angle of deposition, but almost saturating above 60° of the deposition angle.

3.2 Effects of Ambient Gas

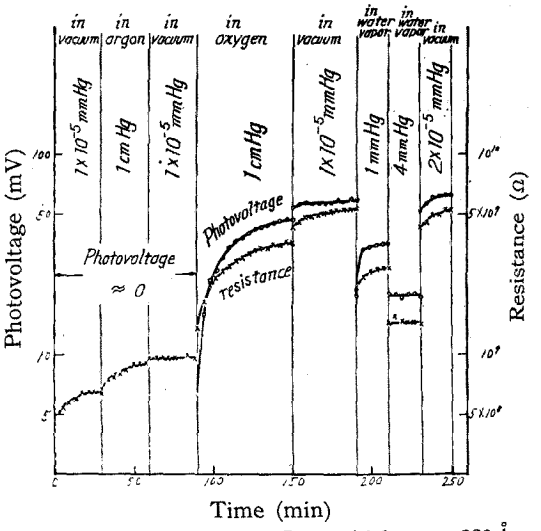
Photovoltage does not necessarily appear by mere oblique angle deposition; exposure to air or oxygen is needed. **Fig. 4** shows the effect of the atmosphere. The film was left after the deposition as it was, then it was exposed to air, put back into vacuum, and these procedures were repeated. The photovoltage does not appear immediately after the deposition in vacuum but it instantly appears when the film is exposed to air, and when the film is put back into vacuum the photovoltage increases to a larger extent. The photovoltage abruptly drops to a small value by a slight re-deposition from the same evaporator, but it recovers to the original value by exposure to air and by re-evacuation. This shows that the source of the photovoltaic effect exists close to the film surface.

Fig. 5 shows the effects of argon, oxygen and water vapor. Photovoltage does not appear immediately after the deposition in vacuum and is not affected by exposure to argon. But it grows by exposure to oxygen. Water vapor reduces the voltage which is easily recovered by evacuation. **Fig. 6** shows the



Deposition angle=45°, Film thickness=810 Å,
Film length=6 mm, Film width=4 mm

Fig. 4 Effect of atmosphere. Photovoltage instantly appears as the film is exposed to air, and it increases when the film is put back into vacuum. The photovoltage abruptly drops to a small value by a slight re-deposition, but it recovers by exposure to air and by re-evacuation.



Deposition angle=45°, Film thickness=320 Å,
Film length=4 mm, Film width=4 mm

Fig. 5 Effect of argon, oxygen and water vapor. The photovoltage does not appear immediately after the deposition in vacuum and is not affected by exposure to argon. It grows by introduction of oxygen, but water vapor reduces it considerably.

variation of the photovoltage by the pressure of oxygen. A fairly large photovoltage appears

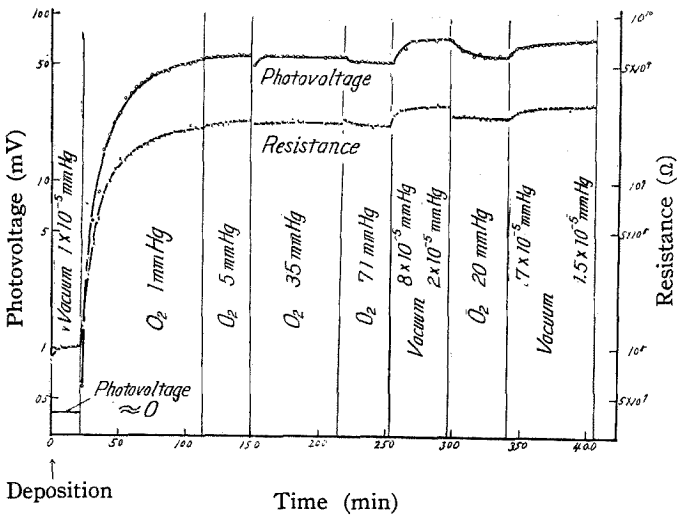


Fig. 6 Variation of photovoltage by oxygen pressure.

even at low oxygen pressure if the film is kept for a long time in oxygen. The reason why the photovoltage is higher in vacuum than in air may be attributed to the presence of water vapor in air, for the photovoltage is suppressed by water vapor which is however removed by evacuation.

3.3 Re-deposition

(1) Re-deposition from the Same Direction

After germanium was obliquely deposited on a substrate, the film was once exposed to air then again subjected to vacuum and the photovoltage was measured. Re-deposition from the same direction by the same evaporator, exposure to air, evacuation and measurement were repeated several times. **Fig. 7** shows the results obtained. The substrate and evaporator were left undisturbed during this experiment. If the deposition is made in a single process, the thicker the film, the lower the voltage as will be described later, but in the present case, the photovoltage did not decrease in the beginning even though the thickness was increased. This shows that the photovoltaic elements, once formed on the surface by exposure to air, do not disappear by the re-deposition on them. If we assume that the effect of photo-excitement is most pronounced on the photovoltaic elements formed on newly deposited surface, quicker falling-off of photovoltage generated by illumination from back of the film than that generated by illumination from the front as the film thickness is increased is explainable.

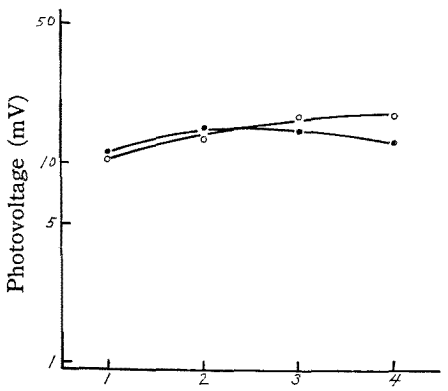


Fig. 7 Effect of re-deposition from the same direction to the photovoltage.
Deposistion angle=45°
Film length=4 mm
Film width=4 mm
Film thickness: mean deposited thickness per one deposition=240 Å
The film is illuminated
{ from behind the substrate. •
{ from the front. ○

(2) Re-deposition from Different Directions

Two evaporators A and B were provided in the vacuum chamber as shown in **Fig. 8** and the deposition was first made with A. After the film was once exposed to air and again subjected to vacuum, the photovoltage was measured. Subsequent repeated depositions with the evaporator B, exposures, evacuations and measurements were made. The results are shown in **Fig. 9.** When the light was illuminated from the front, the photovoltage changed its polarity as the depositions from the different direction was continued. From this result it is concluded that the polarity of the photovoltage depends upon the direction of the deposition on the surface. However,

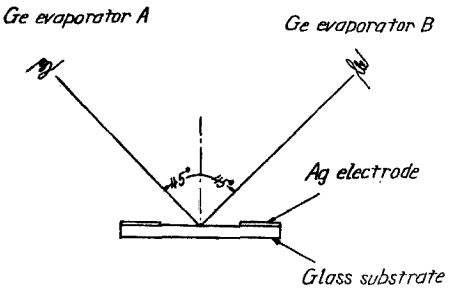
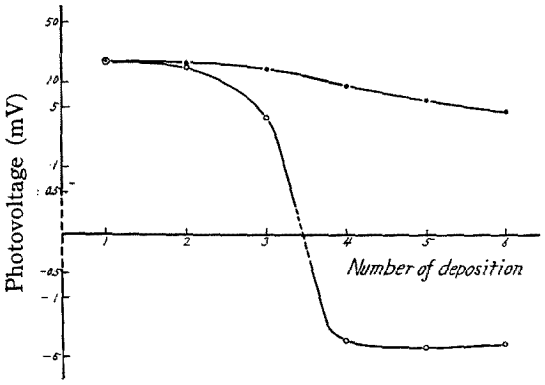


Fig. 8 Schematic arrangement for deposition from different directions.



Deposition angle
1: 45°
2～6: −45°
Film length=4 mm
Film width=4 mm
Film thickness: mean deposited thickness per one deposition=100 Å
The film is illuminated
{ from behind the substrate. •
{ from the front. ○

Fig. 9 Effect of re-deposition from different direction on the photovoltage. The first deposition was made with the evaporator A in Fig. 8, and subsequent repeated re-depositions were made with the evaporator B. The polarity of photovoltage originated by illumination from behind the film remained unchanged but it reversed after several re-depositions by illumination from the front.

reversal of the polarity did not occur when the film was illuminated from behind. This is probably because the light, after being weakened by absorption of the film, reaches the surface of the film, therefore the effect of deposition from the different direction does not appear sufficiently, leaving the first deposited film to be the chief cause of the photovoltage.

3.4 Considerations on the Effect

Kallman et al[4] in their study on obliquely deposited thin films of germanium and silicon proposed two origins responsible for photovoltage. One is the inhomogeneous photo-excitation in crystallite. The surface layer and the interior of crystallite are different in many respects, especially the upper surface which is considered oxidized to some extent. When the film is illuminated by light, the charged carriers (electrons and holes) are generated in the surface layer and also in the interior by photo-excitation. But the recombination rates of two carriers in surface layer and interior are different and the mobilities of electron and hole are also different which may cause the voltage to develope in every crystallite. If all crystallites are obliquely deposited on the substrate, these voltages will have a component parallel to the substrate surface. If the cancellation of the voltage across the contacts between the crystallites is partial, these minute voltages will be summed up along the length of the film, and a large voltage will appears between both ends. If this mechanism is chiefly responsible for the generation of high photovoltage, the reversal of the polarity of photovoltage by the change in direction of light incident on the film should be expected. This reversal was seen in the case of silicon thin films in the experiments by Kallmann et al., but in the case of germanium thin films this was not found either in their experiments or in our experiments.

The second origin proposed by Kallmann et al. is the photo-excitation at the surface layer, the detail of which was not given by them. But this consideration is acceptable for our experiments. If the origin of photovoltaic effect is due to the large recombination rate of two carriers in the oxidized surface layer, the photovoltages after successive re-depositions from the same direction should suddenly decrease because the oxidized layers are enveloped one by one in the crystallite during the re-depositions. But, as shown in **Fig. 7** this tendency was not seen. On the other hand, in the experiment of re-deposition of the case of **Fig. 4** the photovoltage suddenly decreases by a slight re-deposition from the same direction, yet it easily recovers to the original values by exposure to air and by re-evacuation. This shows that the site of origin of photovoltage is in the surface layer of film.

Now, our considerations are as follows. Goldstein and Pensak[1] used an island model for the explanation of the photovoltaic effect of obliquely deposited film of CdTe. In the present paper, the same model is employed for the structure of the film itself. Although it is not safe to apply theories on large crystals to a germanium thin film composed of numerous micro-cristallites, the following discussions are made based on the existing theories, for there is no alternative.

Because of the magnitude of the photovoltage, a model of aligned array of many pho-

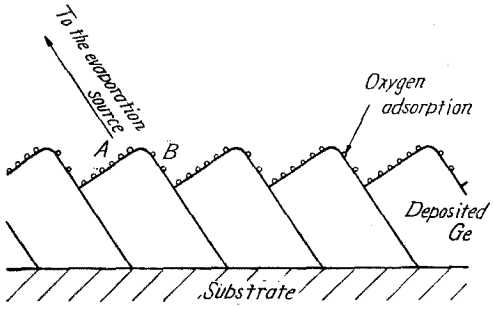


Fig. 10 Schematic representation of obliquely deposited germanium film showing the directional anisotropy in film growth. The film is composed of numerous crystallites arranged with a definite orientation. The oxygen is adsorbed on the film, but its extent is different for different crystallite surfaces.

tovoltaic elements is required. We assume that the film structure is as shown in **Fig. 10.** That is, the atoms that were evaporated from the source and reached the surface of the substrate in the beginning of the deposition move over the surface until they meet and form colonies. When such colonies have grown to certain sizes, the atoms begin to form lattices and make numerous nuclei of the crystal growth. Subsequently, the atoms which have come onto the substrate arrange themselves on those nuclei and finally numerous micro-crystallites are formed. During this formation of crystallites, all the atoms come flying from the direction of the evaporator, so all the crystallites grow in this direction and take a definite orientation. As their growth proceeds, they begin to touch one another side by side forming boundaries.

When a film is placed in oxygen atmosphere, oxygen will be adsorbed on the surface of every crystallite and a layer of P-type will be formed. It is further assumed that the surface facing the evaporator and the side surface of a crystallite have a different tendencies for oxygen adsorption. Then it is not hard to imagine that the extent of this P-type formation will be different for the two surface layers. In **Fig. 10,** the surface layer of a crystallite facing the evaporator is named A and the side surface is named B. If we assumed that the surface layer A is of more P-type than the surface layes B and the positions of Fermi-level in them are somewhat different, the energy band over the film surface is considered as shown in **Fig. 11.** At the contact

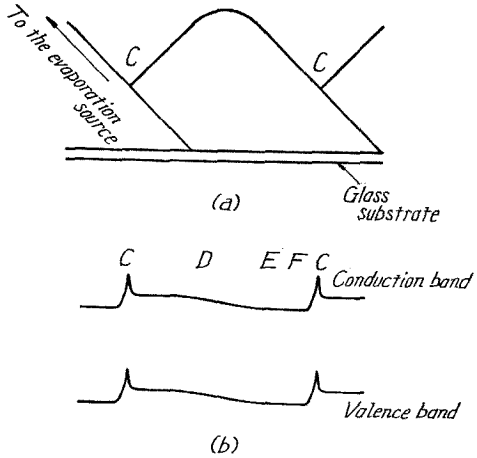


Fig. 11 One of the crystallites of obliquely deposited germanium film (a), and the energy band over the surface layer (b). Asymptotic warping of the energy band occurs at the grain boundary.

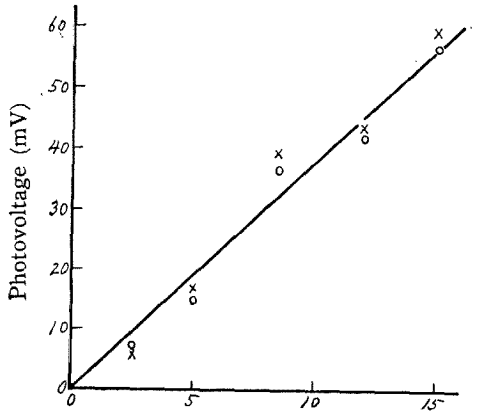
between surface layers A and B, there exist a grain boundary. It is supposed that the assymmetric warping of the energy band occurs on each side of the grain boundary, because, on the two sides, the characteristics of the surface layer itself and the extent of oxygen adsorption are different. When the film is illuminated by light of which quantum energy is larger than the energy gap between the valence band and the conduction band, hole-electron pairs will be generated. If hole-electron pairs are generated in the transition region, excited electrons in the conduction band flow to the lower side in the band, and the holes in the valence band flow to the upper side in the band. So, a carrier concentration difference occurs in the transition region giving rise to the origin of photovoltage. In the case of **Fig. 11 (b)**, some photovoltage is generated by light incident between C–D–E with the polarity by which the voltage on the side of E becomes negative, and also some photovoltage is generated between E–F –C with the polarity by which the voltage on the side of E becomes negative. These photovoltages have opposite polarity, and they are cancelling each other. But this cancellation is imperfect because the warping of the energy band on the two sides of C is asymmetric, so a minute photovoltage remains. As obliquely deposited film is composed of numerous crystallites arranged with definite orientation, so it follows that a minute photovoltage of

every crystallite is summed up along the length of the film and a large photovoltage is observed between two electrodes at both ends.

4. Some Electrical and Photoelectrical Properties

4.1 Film Length

When photovoltages are measured on films deposited at a definite deposition angle on substrates but with different film length, the photovoltage generated is proportional to the film length as shown in **Fig. 12.**

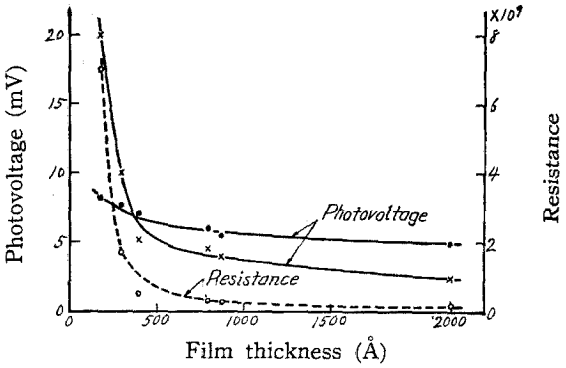


Film width=7 mm
Film thickness=700 Å
Deposition angle=45°
(at the center)
The film is illuminated
{ from behind the substrate. ×
{ from the front. ○

Fig. 12 Photovoltage *vs.* film length. The photovoltage is proportional to the film length.

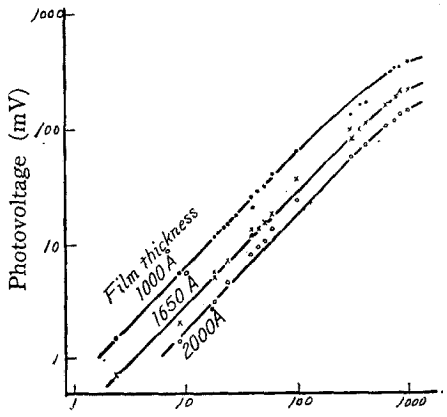
4.2 Film Thickness

Some substrates with the same spacing distance between electrodes were placed in a circle and the deposition was made obliquely at the same time from a evaporator placed above the center of the circle. During the deposition, a shielding plate was inserted one by one in order to prepare the samples with different film thickness but with the same deposition angle. The relation between the film thickness and the photovoltage was thus examined. The results are shown in **Fig. 13.** When the deposition angle is the same, the photovoltage decreases as the film thickness increases, because of the increase in the short-circuiting effect with the film thickens. When the film is thin, illumination from behind the substrate gives higher photovoltage than when the illumination is from the front. This may be explained as follows: as the obliquely deposited surface of the film is rough, so the incident light is considerably scattered on the film surface causing the difference in the photovoltage mentioned above. However, it is assumed that the photovoltage is generated on the upper surface of the film. Therefore,



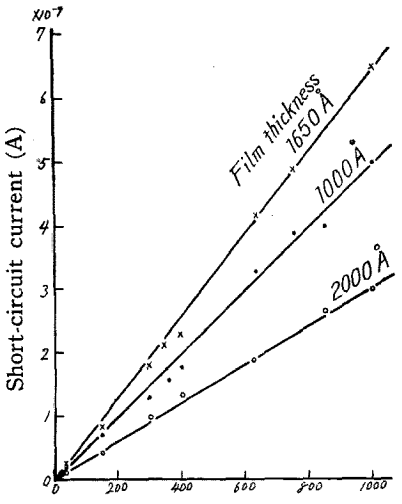
Film length=2.5 mm
Film width=2 mm
Deposition angle=45°
The film is illuminated
{ from behind the substrate. ×
{ from the front. ○

Fig. 13 Photovoltage *vs.* thickness of film deposited at a definite deposition angle. The photovoltage decreases as the film thickness increases. Film resistance *vs.* film thickness is also shown.



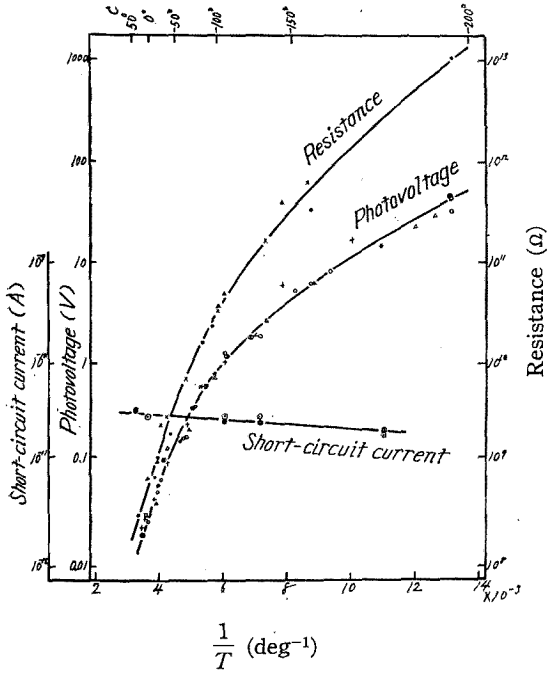
Deposition angle=45°
Film length=4 mm
Film width=3 mm

Fig. 14 Photovoltage *vs.* relative light intensity L; $L=1$ corresponds to about 60 lux. The light flux was attenuated by neutral filters. The photovoltage is proportional to the light intensity when the light is weak.



Deposition angle=45°
Film length=4 mm
Film width=3 mm

Fig. 15 Short-circuit photocurrent *vs.* light intensity for different film thickness.



Deposition angle=45°
Film thickness=520 Å
Film length=4 mm
Film width=5 mm

Fig. 16 Photovoltage, photocurrent and resistance *vs.* temperature. In the vicinity of room temperature, the photovoltage is in proportion to the resistance, but this proportionality is broken at low temperature. The photocurrent has a weak temperature dependence.

when the film is thick, the light incident on the back is absorbed before it reaches the surface, and therefore the photovoltage is smaller when illuminated from behind than illuminated on the surface.

4.3 Light Intensity

As shown in **Fig. 14,** the photovoltage is proportional to the light intensity when the light is weak. However, when the light intensity becomes large, the photovoltage does not vary proportionally to the light intensity; its rate of increase decreases. **Fig. 15** shows the relation between the light intensity and the short-circuit photocurrent. The former is proportional to the latter.

4.4 Low Temperature

Measurements on the photovoltage and other properties were made on a film in vacuum after being exposed to air at the temperature ranging between the room temperature and liquid nitrogen. The results are shown in **Fig. 16.** The photovoltage V_p and the resistance R show a steep increase with the decrease in temperatuse, but the short-circuit photocurrent I_s has a weak temperature dependence. In the vicinity of room temperature, photovoltage is proportional to the resistance and the relation $V_p=RI_s$ approximately holds. At low temperature, however, this relationship does not hold any longer. The rate of increare in photovoltage is less than that in resistance.

5. Summary and Conclusions

The results of the present investigation are summarized as follows:

The germanium film prepared by vacuum evaporation and deposited at an oblique angle of incidence onto a substrate exhibits a high photovoltaic effect in which the positive voltage appears on the side opposite to the evaporator. For such a phenomenon to appear, oblique deposition of germanium and exposure to air or oxygen are necessary, while inert gas does not affect photovoltage. Island model consisting of an aligned array of many photovoltaic elements and the adsorption of gas on the crystallite surfaces well explains the photovoltaic effect. Photovoltage decreases when the film thickness increases, and is proportional to the length of the film. When the intensity of light is weak, the photovoltage

is proportional to it. But, when the intensity of light is strong, this relationship does not hold and the rate of increase in the photovoltage becomes small. When the temperature is lowered, the photovoltage increases to a large extent. In the vicinity of room temperature, resitance of the film and photovoltage have the same temperature dependency, hence they are proportional to each other, but at lower temperature, the rate of increase of the photovoltage becomes smaller than that of the resistance. Short-circuit photocurrent is proportional to the intensity of light and has a weak temperature dependence.

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The Analytical Solution of Anastigmatic Optical Lenses (II)
—Single Thick Lenses—

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Abstract

The shapes of single thin lenses designed by repeated ray-tracing differ remarkably sometimes from those calculated by the formula given in Part 1. Therefore, by taking into account of the thickness of the lens, which seems to be the main reason of this discepancy, an analytical study is made to render single thick lenses anastigmatic in the Seidel region by the application of Zinken-Sommer's condition.

When the object plane is placed at infinity or at the anterior focal plane of the lens, the anastigmatic condition turns into equations of the fifth degree of refractive power of the first surface. But it is of the seventh degree when the magnification of the image is taken as a parameter, and of the sixth degree when the distance of the object plane is taken as a parameter.

The possibility of finding the required shape or shapes of the lens rests on the solution of these equations.

1. Introduction

In the previous paper,[1] a study was made to determine analytically the shape of single thin lenses corrected for astigmatism in the Seidel region. But when anastigmatic spectacle lenses with finite thickness are concerned, designed shape by repeated ray-tracing differs often remarkably from that calculated by the formula obtained in the previous paper. The main reason of this discrepancy seems to be due to the finite thickness of the lens actually designed. So the thickness of the lens is taken up in this paper.

Let us consider a single thick lens of focal length f' made of material with refractive index n against the air and of finite thickness d, equipped with a pupil at a given position behind the lens forming anastigmatic image of a given object plane.