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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

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SILICON FILMS WITH ANOMALOUSLY LARGE PHOTOVOLTAGES

1. Contrary to the simple band scheme, which limits possible photovoltages* to values of the order of kT/q for homogeneous semiconductors, and to the value of the forbidden-band width ΔE for p–n junctions, Starkiewicz, Sosnowski, and Simpson (2,3) found in thin PbS layers $V_\phi \approx 2 \div 3$ V at $\Delta E \approx 0.4$ V (4) (see also (5–7)). In a considerably sharper form, the effect of the appearance of anomalously large photovoltages ($\sim$ 100 V/cm at room temperature and $\sim$ 1000 V/cm at nitrogen temperature) was observed in CdTe films by Pensak and Goldstein (8–10). Anomalously high photovoltages (a.p.v.) also arise in some other semiconductor films (Sb_2Se_3, Sb_2S_3, etc. (11,12)), as well as in ZnS single crystals (13–15). The question of the nature of a.p.v. is discussed both in the articles cited above and in certain other papers (see, for example, (16–22)); however, it has not yet received a completely reliable explanation.

Fig. 1. Spectral dependence of the light absorption coefficient $k(\lambda)$. Solid curve–literature data; points–film No. 9

Fig. 2. Spectral dependence of the short-circuit current (film No. 1)

About three years ago a report appeared by Kallmann et al. (23) that, with a special deposition technology, a.p.v. can also be generated in thin germanium and silicon films. The possibility of studying the a.p.v. effect in such semiconductor materials as Ge and Si, which are the best studied physically, chemically, and crystallographically, is very promising both for understanding the nature of the phenomenon and for its applications. However, after paper (23) only two works devoted to germanium a.p.v. films (24,25) appeared in print, and there

Fig. 3. Change of V_ϕ and R under illumination (film No. 3). The arrow marks the beginning of cooling of the film.

Figure 3: Fig. 3. Change of V_ϕ and R under illumination (film No. 3). The arrow marks the beginning of cooling of the film.

is not a single report on the preparation and study of silicon a.p.v. films. The reason is apparently connected with the difficulties of reproducing the technological procedures briefly described in the article [23].

The method we have used also makes it possible to obtain silicon films which, under illumination, develop anomalously high photovoltages. Below we describe the procedure and present the first results of the investigation of the a.p.v. Si films obtained.*

2. The starting material was single-crystal p-type silicon with $\rho \sim 1500\ \Omega \cdot \text{cm}$. After preliminary treatment (etching in $HF \cdot HNO_3$, washing in distilled water, washing in acetone, again in distilled water, and drying), a piece of silicon (~ 0.1 g) was placed in a specially made beryllium oxide crucible [26, 27]. Deposition was carried out onto a quartz plate ($1.5 \times 0.7 \times 0.2$ cm), previously washed in acetone, alcohol, and distilled water and dried in air,

Fig. 3. Change of V_ϕ and R under illumination (film No. 3). The arrow marks the beginning of cooling of the film.

The crucible was heated by Joule heat, and the quartz substrate was heated by the thermal radiation of the crucible. Temperature measurements were made with a Pt—Pt · Rh thermocouple. The plate was positioned at a distance of about 2 cm at an angle of $40 \div 45°$. The crucible temperature was 1300–1450°, the substrate temperature about 500°, and the vacuum $10^{-5} \div 10^{-6}$ torr. Deposition was carried out both by sublimation of the solid phase of Si and by evaporation of the melt. The deposition time was determined by the required film thickness; for a thickness on the order of several microns, the deposition time was 10–15 min. The film was cooled to room temperature in vacuum, after which air was admitted into the system.

3. Photovoltages in the films were generated by illuminating them with a 500-watt reflector lamp, which produced an illuminance of 50,000 lx at the surface of the film. The photovoltages were measured with S-95 and S-50 static voltmeters. Pressure contacts were used; in some cases the contacts were pressed directly to the film, and in others to silver or aquadag electrodes deposited on the films. The results did not depend on this. To measure the resistances of the films

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* According to (1), upon illumination of a semiconductor no definite photo-e.m.f.'s arise, and one can speak only of photovoltages.

Fig. 4. Current-voltage characteristics.

Figure 4: Fig. 4. Current-voltage characteristics.

an MOM-4 megohmmeter was used. The resistances of the films were also determined from current-voltage characteristics.

The measurement results are given in Table 1. The voltages V'_ϕ were taken directly during illumination of the films, and V''_ϕ during cooling of the films under illumination by blowing with a stream of air at room temperature.

* A report on this work was made at the Third All-Union Conference on Photoelectric Phenomena in Semiconductors in Kiev in October 1963.

Since the internal resistance of the films is large and in some cases comparable with the input resistance of the measuring instrument, V'_ϕ and V''_ϕ are smaller than the open-circuit photovoltage.

Table 1

Film No.	1	2	3	4	5
V'_ϕ, V	8	14	20.5	7	5
V''_ϕ, V	14	18	73	12	6
R, ohm	$6 \cdot 10^{11}$	$2 \cdot 10^{12}$	$1.5 \cdot 10^{14}$	$2 \cdot 10^{13}$	10^{14}

Figure 1 gives a typical curve of light absorption in the films obtained by us. The experimental results agree well with the data published in the literature (see, for example, ([28])) for $k(\lambda)$ in silicon. Bringing the curves into coincidence at $\lambda = 600$ mμ made it possible to determine the film thickness (about 5 μ).

Fig. 4. Volt-ampere characteristics. 1 –film No. 3, $I = 0$, $R = 1.5 \cdot 10^{14}$ ohm; 2 –film No. 3, $I = 50\,000$ lx, $R = 1.2 \cdot 10^{13}$ ohm; 3 –film No. 2, $I = 0$, $R = 2 \cdot 10^{12}$ ohm; 4 –film No. 2, $I = 50\,000$ lx, $R = 5 \cdot 10^{11}$ ohm. The left-hand scale is for curves 1 and 2, the right-hand scale for curves 3 and 4.

Figure 2 shows the experimental curve of the spectral distribution of the short-circuit current in a.c.v. silicon films, recalculated per unit incident energy. Measurements of the light absorption were made on an SF-4 spectrophotometer. In recording the curves of the spectral distribution of the short-circuit current, a lamp of known color temperature was used, and the optical part of the SF-4 served as the monochromator.

Illumination, as well as the heating accompanying illumination, causes a change in the ohmic resistance R. Since the photovoltage taken from a semiconductor cannot be represented as the difference between a photo-e.m.f. and the internal voltage drop ([1]), the relation between V_ϕ and R has a complex character and reflects features associated with the nature of the a.c.v. in semiconductor films. As a first stage in studying these features, parallel measurements of the photovoltages V_ϕ and the resistances R under illumination of a.c.v. films were carried out.

The results for one of the films (No. 3) are given in Fig. 3. Cooling was begun after the photovoltage of the uncooled film had reached saturation. As can be seen from Fig. 3, the growth of R after the start of cooling is accompanied by an increase in V_ϕ, which indicates a stronger temperature dependence of the circulation electromotive forces $E(I, T, J)$ in comparison with the temperature dependence of the film resistance $R(I, T)$. Here I is the in-

light intensity, T is temperature, J is current. The kinetics of the change in V_ϕ and R with time is complicated by the inertia of the measuring circuit (rC is on the order of several minutes), with which, apparently, is also associated the increase in the measured photovoltage accompanying the drop in the resistance of the film at the initial stage of illumination.

Figure 4 gives the current-voltage characteristics of silicon a.p.n. films in the dark and under illumination. All the characteristics are ohmic, at least up to fields of 10^3 V/cm. The voltages were supplied from a UIP-1 and measured directly at the output of the UIP. The currents were measured with an EMU-3 electrometric amplifier with load resistances $r \ll R$.

The results presented above show that, by means of the method described in the present article, it is possible to obtain silicon films that, under illumination, give anomalously large voltages. The results of a more detailed experimental and theoretical study of these films will be published separately.

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Note: Figure translations are in progress. See original paper for figures.