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Abstract

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A.P.V. Films Obtained by Sublimation of Si Atoms from the Surface of a Current-Carrying Silicon Plate

1. Thin silicon films that develop anomalously large photovoltages (a.p.v.) upon illumination were obtained by Kalman et al. (1), and subsequently by Adirovich and Yuabov (2). Below we describe another method for obtaining such films and the first results of their investigation.

Beginning with the first works of Peshak and Goldshtein (3–5) on a.p.v. films of cadmium telluride, the literature has emphasized the fundamental importance of oblique deposition of films onto a substrate; theoretical ideas concerning the formation of rectifying or Dember microregions, which together give anomalously large photovoltages, are associated with this. To form such films, the methods being developed tended toward the creation of a "point" source (i.e., one small in comparison with the dimensions of the substrate) and directed atomic beams.

The configuration and dimensions of the source in the method described below create substantially different conditions for film formation during deposition. Films are applied to substrates by sublimation of silicon from the surface of a silicon plate heated by a current passing through it. The dimensions of the substrates and their distance from the evaporator (the silicon plate) are commensurate with its dimensions; as a result, deposition is produced by atomic beams incident on the substrate at different angles, without a clearly pronounced angular asymmetry. In this case, approximately 70% of the silicon films obtained in this way give anomalously large photovoltages of the order of several tens of volts at room temperature.

2. In our work, silicon plates ($\sim 30 \times 3 \times 0.5$ mm), cut from a p-type single crystal with $\rho \sim 1$ ohm · cm, served as evaporators. Such a plate was clamped between two electrodes made of spectrally pure carbon and was placed along the axis of a thin-walled copper cylinder, on the inner surface of which 5-8 quartz or glass substrates ($40 \times 25 \times 1$ mm) were arranged. Heating of the silicon plate was carried out by a current passing through it. The substrates were heated by the thermal radiation of the plate.

In order to be able independently to vary the temperatures of the evaporator and the substrates, we used copper cylinders of different diameters (from 45 to 78 mm). The temperature of the substrates was measured with a copperconstantan thermocouple and was $70 \div 250^\circ$C. Deposition was carried out in a vacuum of $3 \div 4 \cdot 10^{-6}$ torr.

The silicon plate was heated gradually by smoothly and slowly increasing the applied voltage. With the aid of a specially selected series resistance, voltage control on the initial (OA) section and current control on the falling (BC) sections of the current-voltage characteristic were ensured (curve 1 in Fig. 1). This same load resistance and the heat-transfer process limit the region of instability (AB in Fig. 1) and ensure stabilization of the current regime after the onset of thermal breakdown.

For investigation of the temperature dependence of the deposition conditions and of the properties of the films, with the aim of finding the optimal technological re—

precise measurements and continuous monitoring of the temperature of the silicon plate are of fundamental importance. This is also necessary for carrying out deposition processes in the optimum regime found. Since pyrometric methods do not provide sufficient accuracy in determining the temperature, and the use of thermocouples involves a number of considerable difficulties, we used the silicon plate itself as the temperature-measuring device.

Since in the intrinsic-conduction region the specific resistance of the material ρ is a single-valued function of the temperature T, a conditional characteristic of the evaporator temperature at a given V may be $\rho(V)$, determined from the current-voltage characteristic and the data on the geometry of the silicon plate (curve 2 in Fig. 1).

Fig. 1 Fig. 2

Fig. 1

Fig. 2

For the calibration of such an intrinsic thermometer on an absolute temperature scale, pieces of aluminum, germanium, and copper were placed on plates of known geometry, and the values of ρ and T corresponding to their melting temperatures were recorded. The reference points thus obtained—Al 933°K; Ge 1231°K; Cu 1356°K—as well as a fourth point corresponding to the beginning of melting of the silicon itself (1693°K), are shown in Fig. 1. As is seen from the figure, these results make it possible, with sufficient confidence, to draw the curve

$$\rho = \rho_0 \exp\left[T_1\left(\frac{1}{T} - \frac{1}{T_0}\right)\right], \tag{1}$$

where the values of the parameters determined from the reference points are

$$T_1 = 6850^\circ\text{K}, \qquad E_g = 1.18\ \text{eV}, \qquad \rho_0 = 3.4 \cdot 10^5\ \Omega \cdot \text{cm}, \tag{2}$$

which agrees well with the latest data for silicon ([6],[7]):

$$E_g = 1.21 \text{ eV}, \qquad T_1 = \frac{E_g}{2k} = 7014^\circ\text{K}, \qquad \rho_0 = 2.3 \cdot 10^5 \ \Omega \cdot \text{cm}. \qquad (3)$$

Let us note that the validity of a formula of the form (1) for the intrinsic conductivity of silicon up to the melting temperature was experimentally proved by Mokrovskii and Regel' ([8]), the values of ρ at the melting point obtained by us and in ([8]) coinciding ($2.3 \cdot 10^{-3}\ \Omega \cdot \text{cm}$).

These results make it possible, with sufficient confidence, to use graph 3 in Fig. 1 to determine the absolute temperature of the silicon plate from its specific resistance, i.e., ultimately, from the current-voltage characteristic.

Putting into correspondence the points of curves 1 and 3, we establish the relation between the current passing through the silicon plate and its temperature (curve 4). In Fig. 1 the arrows show the sequence of operations in the graphical ...

construction of curve 4 for determining the temperature at any point of the current-voltage characteristic.

3. A procedure, in some respects similar to that described above, was used by Kilgore and Roberts (^9) for depositing chemically active semiconductor surfaces. To obtain a.p.n. films there is no need for such a high vacuum ($\sim 10^{-9}$ torr) or for such thorough cleaning of the surface of the initial silicon as in the deposition of chemically active films. An important advantage of methods based on the evaporation of silicon from the surface of plates or filaments is that these methods readily make it possible to obtain films of large dimensions. In particular, the dimensions of the films obtained in the present work were not limited by the capabilities of the method, but were determined only by the size of the substrates and their distance from the evaporator. The preparation by this method of a.p.n. films of large area and their investigation will be described separately.

A significant disadvantage of methods based on the sublimation of atoms from plates or filaments heated by current is the long duration of the deposition process. In the work of Kilgore and Roberts, and in our first experiments, the time required to prepare a film of thickness $2 \div 3\,\mu$ amounted to several tens of hours. This time can be substantially reduced by carrying out the deposition process at the highest possible temperature that does not lead to melting of the plate by the current. As a sensitive and low-inertia temperature indicator, allowing the deposition process to be conducted reliably in such a critical regime, we used the ion current between the evaporator and a copper cylinder. Figure 2 shows the dependence of the ion current i on the through current through the plate I at a voltage on the cylinder of -600 V (curve 1). In the left-hand quadrant, using the same graphical construction as in Fig. 1, the dependence of i on the temperature of the plate T (curve 2) is shown.

Table 1

No. of sample	R, ohm	d, μ	V_a , V	T , °C	T , °C
1	$5 \cdot 10^{13}$	1.25	38	1170	168
2	$2 \cdot 10^{12}$	3.02	24	1170	150
3	$7 \cdot 10^{12}$	1.42	35	1170	230
4	$1 \cdot 10^{12}$	2.3	42	1240	145
5	$1.5 \cdot 10^{13}$	1.16	70	1240	78
6	$1.8 \cdot 10^{12}$	2.84	40	1270	211
7	$2 \cdot 10^{13}$	1.37	30	1270	195
8	$1 \cdot 10^{13}$	0.98	72	1320	242
9	$2.7 \cdot 10^{12}$	1.43	54	1320	242
10	$4 \cdot 10^{12}$	1.54	36	1320	90

As is seen from the figures, the accuracy of the fixed value of the deposition temperature increases, on going from measurement of I to measurement of i, by a factor equal to the ratio $\tan\beta/\tan\alpha$. Monitoring the ion currents enabled us to shorten the process of depositing a.p.n. silicon films ($d \sim 2 \div 3\,\mu$) to 3 h, and the possibilities of the method are still far from exhausted.

We note that simultaneous measurement of the ion and through currents in semiconductors, when the latter are used as a kind of thermometer, may serve as a method for studying the regularities of evaporation of atoms from the surface of semiconductors. Establishing the relation between the overall rate of sputtering of the material and the density of the ion current at different temperatures will, in particular, make it possible to obtain films with a prescribed thickness.

4. In all, more than 50 films were obtained and investigated. For 10 of them, Table 1 gives the values of the resistance R, the thickness d, and the voltage V_a , as well as the temperatures of the silicon plate T and of the substrate T during deposition. R and d were measured in the same way as in (^2, ^3). The values of V_a were obtained at an illumination of 30,000 lx and room temperature. The measurements were made with a voltmeter assembled on a 6Zh1Zh tube, operating in the inverse mode (^11).

In their properties the films obtained are similar to those described in (^2, ^10). According to electron-diffraction data obtained on several films, they possess an amorphous structure.

It should also be noted that, for different films obtained in one and the same experiment, the maximum value of V_{afn} occurs in different directions, varying from longitudinal (parallel to the axis of the evaporator) to transverse. For each film there is a direction along which $V_{afn} = 0$.

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