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Abstract

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MICROPHOTOBATTERY OR PHOTOCELL?

1. The theory of the effect of anomalously large photovoltages (a.l.p.) in semiconductor films has not yet received a quantitative development, and even in its qualitative interpretation different authors are far from unanimous. However, with a single exception, all investigators treat a.l.p. films as complex devices consisting of a large number of series-connected microscopic ($10^{-4} \div 10^{-5}$ cm) regions which, upon illumination, create photoelectric voltages $v_i \lessgtr kT/q$. In other words, the a.l.p. effect is interpreted as the result of the addition of a large number of small photovoltages generated in individual microphotocells, while the a.l.p. film is regarded as a microphotobattery created in a single technological process of depositing semiconductor material on a substrate. The divergence of views arises in the question of the physical nature of the microphotocells forming the a.l.p. film. Various authors believe these to be p–n junctions ([1–6]), Dember microregions ([7,8]), packing defects at the phase boundary ([9,10]), or microregions with an external photoeffect ([1]).

The above-mentioned exception is the work of Brandhorst and Potter ([11]). According to the views developed by these authors, a semiconductor a.l.p. film is a single high-resistance photocell, and its anomalous properties are due to traps that create a concentration gradient of minority charge carriers localized at sticking levels. From the formula obtained in ([11]) (the notation refers to the p-type):

$$V = \frac{kT}{q}\,\frac{n_{\text{loc}}}{p_0}\bigg|_{x=0}^{x=l} \tag{1}$$

it follows that a sufficiently large, but realistically possible, concentration of electrons on traps (for example, $n_{\text{loc}}/p_0 \sim 10^4 \div 10^5$), concentrated at one of the ends of the film, can lead to the appearance of photovoltages of the order of $100 \div 1000$ V. Reviewing the experimental data, Brandhorst and Potter come to the conclusion that the totality of known facts is in good agreement with the concept they develop.

Thus, after the publication of paper ([11]), a divergence of views arose in the theory of the a.l.p. effect on the basic question: whether the a.l.p. film is a microphotobattery or a single complex photocell.

2. Calculation of photovoltaic effects invariably leads to expressions of the form of the product kT/q by a logarithmic function of the concentrations of free carriers (see, for example, ($^{12-14}$)); however, the theory of photovoltages has until now ignored the possible role of sticking levels. Meanwhile, the regularities of other phenomena in solids (for example, high-resistance polarization (^{15}) or the electret effect (^{16})) indicate that charges localized at these levels can create sufficiently high voltages. Brandhorst and Potter believe that their accounting for the field of localized carriers in a photocell with a nonuniform distribution of traps leads to an analogous conclusion.

and for photovoltages. However, this conclusion is erroneous. It is connected with the unlawful extrapolation of the particular solution (1), obtained in (11), to the range of values $|n_{\text{loc}}(l) - n_{\text{loc}}(0)| \gg p_0$, for which this solution is inapplicable.

Let us consider the initial system of equations in the article (11)

$$\mu p_0 \mathbf{E} = D(\operatorname{grad} p - \operatorname{grad} n), \tag{2}$$

$$\operatorname{div} \mathbf{E} = \frac{4\pi q}{\varkappa}\left[(p - p_0) - (n - n_0) - n_{\text{loc}}\right].$$

The first of these is obtained from the current equation

$$\mathbf{j} = q\mu(bn + p)\mathbf{E} - qD \operatorname{grad} p + qbD \operatorname{grad} n = 0 \tag{3}$$

under the condition $b \equiv \mu_n/\mu_p = 1$ and

$$n_0 + (p - p_0) + (n - n_0) \ll p_0. \tag{4}$$

Brandhorst and Potter solve the system of equations (2) by taking the gradient of both sides of Poisson' s equation and then replacing $\operatorname{grad}(p - n)$ by $\frac{q}{kT} p_0 \mathbf{E}$, according to the first equation (2), which gives as a result

$$\frac{q}{kT} p_0 \mathbf{E} - \frac{\varkappa}{4\pi q} \operatorname{grad} \operatorname{div} \mathbf{E} = \operatorname{grad} n_{\text{loc}}. \tag{5}$$

With a quadratic approximation of the distribution of localized electrons along the film, $n = A + Bx + Cx^2$, equation (5) has a solution of the form

$$E = \frac{kT}{qp_0} \frac{dn_{\text{loc}}}{dx}. \tag{6}$$

Integration of expression (6) leads to formula (1). It is easy to see, however, that solution (6) corresponds to the condition $\operatorname{grad}\operatorname{div}\mathbf{E} = 0$, i.e., to constancy of the space-charge density along the film. In particular, it must be that

$$\left[(p-p_0)-(n-n_0)-n_{\text{loc}}\right]_{x=0} = \left[(p-p_0)-(n-n_0)-n_{\text{loc}}\right]_{x=l}. \tag{7}$$

From (7) and (4) it follows that

$$\left|[n_{\text{loc}}]_{x=0}^{x=l}\right| = \left|[(p-p_0)-(n-n_0)]_{x=0}^{x=l}\right| \ll p_0. \tag{8}$$

Thus it has been proved that V in the Brandhorst and Potter solution (1) not only cannot exceed the width of the forbidden band of the semiconductor E_g, but is limited by the much stricter inequality

$$V \ll kT/q.$$

We note that this result can be obtained by a much more direct route, by directly integrating along the film the field $\mathbf{E}$ determined from the first equation (2).

3. Let us show that the impossibility of the appearance of anomalously large photovoltages caused by the field of charges localized in traps is not connected with the particular assumption of a low generation level and with the fact that traps can capture only minority carriers. Introducing the quasi-Fermi levels F_p and F_n (17), we transform equation (3) to the form

$$\frac{dF_p}{dx} = -b\,\frac{n}{p}\,\frac{dF_n}{dx}, \tag{9}$$

where*

$$p = n_i e^{-(F_p+q\psi)/kT}; \qquad n = n_i e^{(F_n+q\psi)/kT}. \tag{10}$$

* In contrast to Shockley (17), we use a band scheme in which the electron energy, rather than the hole energy, is taken as positive.

Integrating (9) along the film from $x=0$, where we choose the origin for the potential, to $x=l$, where the potential is equal to V, and applying the mean-value theorem, we obtain

$$\Delta F_p = -b e^{(\overline{F_p+q\psi})/kT + (\overline{F_n+q\psi})/kT}\,\Delta F_n. \tag{11}$$

At no real illumination intensities can a degeneracy of the electron or hole ensemble be created in the semiconductor. Consequently, if F_n and F_p are monotonic functions, then it must be that

$$-E_g - qV \leq \Delta F_n \leq E_g - qV,$$

$$e^{-(\overline{F_p+q\psi})/kT-(\overline{F_n+q\psi})/kT}\,\frac{-E_g+qV}{b} \leq \Delta F_n \leq \frac{E_g+qV}{b}\,e^{-(\overline{F_p+q\psi})/kT-(\overline{F_n+q\psi})/kT}. \tag{12}$$

For $V > E_g/q$, the inequalities (12) are incompatible. Consequently, in the Bransky-Potter model the a.ph.v. effect cannot arise at any generation levels.

It is clear that a majorant estimate of V in a model with such an impurity distribution, in which the derivatives of the functions $F_p(x)$, $F_n(x)$ are not sign-constant, can be obtained by dividing into intervals within which both functions are monotonic. Consequently, the a.ph.v. effect certainly cannot arise if, in the semiconductor, regions of rise and regions of fall of the quasi-Fermi levels do not alternate many times. This proves the theorem on the necessity of a battery structure of a.ph.v. films. The theorem of sufficiency and an analysis of the conditions under which regions possessing different properties and alternating in sequence create summing photovoltages will be considered separately, as will the main physical question—what is the nature of the elements forming the film microphotobattery.

In the present article we shall also give a description of two experiments that made it possible to narrow the range of possible hypotheses concerning the physical nature of the microphotoelements forming a.ph.v. films, and to separate the fundamentally important and secondary conditions for the formation of a.ph.v. films from such elements.

4. It was already indicated above that, within the framework of the battery concept, four different hypotheses concerning the physical nature of the a.ph.v. effect have been advanced in the literature. One of them, based on the idea of an external photoeffect from illuminated dendrite edges (^{1}), gives rise to a priori objections connected with the discrepancy between the red edge of the a.ph.v. effect and the red edge of the external photoeffect ($\lambda_{\text{a.ph.v.}} > \lambda_{\text{ext.phot.}}$). However, direct measurements of the work function of a.ph.v. films have not been carried out, and peculiarities of the structure and specific properties of the film surface may cause a shift of the red edge of the external photoeffect. Therefore we carried out a direct experimental test of this hypothesis.

The measurements were carried out on a special setup with an open spark counter of the Bogun-counter type (^{18}), constructed for measuring the exoelectron emission of crystalline phosphors (^{19})*. The setup made it possible reliably to record emission currents of the order of 10^{-18} A, which is 6–8 orders of magnitude smaller than the short-circuit currents in the a.ph.v. films investigated by us. A.ph.v. films of all the materials we investigated were tested: Si, Ge, GaAs, Se, CdTe ($^{20-23}$). Electron emission from the surface of the films was not detected. It was thereby proved that the a.ph.v. effect is due not to external electron emission from dendritic needles, but to a redistribution of charges inside the film.

5. On the basis of fairly extensive statistical material, almost all investigators note that, in order to obtain a.ph.v. films, angular asymmetry during deposition and a thickness gradient of the deposited—

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layer. Do both of these features express some single general property of films, one that is fundamentally important for the occurrence of the a.p.n.-effect (for example, anisotropy of the elements forming the microphotobattery, or anisotropy of the bonds between them), or do they characterize different regularities in the formation of a.p.n.-films? In the latter case, what exactly—the oblique deposition or the gradient of the film thickness—is essential for the occurrence of the a.p.n.-effect?

The answers to these questions are very important for understanding what elements and bonds form a film microphotobattery. Naturally, wedge-shaped films are formed during oblique deposition. However, in some works a.p.n.-films were obtained by deposition carried out without a clearly expressed angular asymmetry: from a "point" source along the normal to the substrate surface [24], and also from the surface of sources commensurate with the dimensions of the substrate and with the distance from the evaporator to the substrate [25].

We set up a direct experiment that made it possible to separate these two features and to determine which of them governs the emergence of a.p.n.-properties in semiconductor films.

Between the accumulation source (a beryllium oxide crucible with an evaporation-surface size on the order of the film length) and the substrate in a vacuum chamber, a screen was installed that was moved by means of an electromagnetic drive parallel to the source surface. By varying the speed of movement of the screen and the inclination of the substrate with respect to the axis of the molecular beam, it was possible independently to control the angular anisotropy of deposition and the thickness gradient of the films, obtaining, in particular, films of constant thickness under oblique deposition and wedge-shaped films under normal deposition. Films of both types were obtained from all the semiconductor materials we investigated. The experimental results make it possible to assert that a.p.n.-films are formed only under anisotropic deposition, independently of the presence or absence of a thickness gradient.

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

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