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Distinction between surface and bulk states in surface-photovoltage spectroscopy

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The effect of localized electron states on the photovoltage at a free semiconductor surface is analyzed. The analysis shows that surface-photovoltage spectroscopy (SPS) is inherently more sensitive to surface states than to bulk states. Moreover, a fundamental difference between the effect of surface and bulk states on the surface photovoltage (SPV) is shown. The analysis demonstrates that the same illumination-induced variation of the population at a surface and a bulk state may result in a significantly different dependence of the SPV on the illumination intensity. Under certain conditions, this difference makes it possible to distinguish between surface and bulk states by means of SPS. Analytical expressions for these relations are obtained under the depletion approximation, and are compared with the results of a numerical simulation. Experimental results obtained from InP samples demonstrate an application of the theory to practical distinction between surface and bulk states.

I. INTRODUCTION

Surface-photovoltage spectroscopy[1] (SPS) is a powerful tool for the investigation of surface electronic structure, which has proven to be an extensive source of information about optically active surface states at clean and real surfaces of various semiconductors, as well as surfaces with monolayer coverage.[2–13] In SPS experiments, the electronic surface states are probed by monitoring the effect of sub-band-gap illumination on the surface potential. The surface potential is modified by carrier generation under illumination, which results in nonequilibrium charge, and is followed by carrier separation and/or recombination in the surface depletion layer.

Although SPS is a well-established qualitative technique, the quantitative interpretation of specific experimental results remains a complicated and often unsolved problem. To date, one of the most fundamental limitations to quantitative analysis has been the inability to distinguish between the surface-photovoltage (SPV) signal due to surface states and local bulk states. Thus, in spite of previous significant theoretical and experimental efforts,[14–17] all quantitative analyses have been based on assumptions as to the nature of the states. More often than not, these assumptions could not be corroborated by experimental evidence.

In this paper, we shall present some general theoretical considerations of SPS experiments, and show that surface and bulk states may, in principle, be distinguished by a straightforward extension of the original SPS technique. This is demonstrated by experiments conducted on InP samples.

II. EFFECT OF ILLUMINATION ON THE SPV

We shall begin our analysis by examining in detail the relation between local electron state charge and the surface voltage. Under the depletion approximation, there is no electric field in the neutral part of the substrate. Consequently $dV/dx|_{x=w}=0$, where w is the width of the depletion region, and V is the built-in potential. We also choose $V(w)=0$, and denote $V(x=0)$ as V_s. Two integrations of Poisson's equation yield

$$V_s=-\int_0^w dx \int_x^w \frac{\rho(\xi)}{\varepsilon} d\xi \ , \tag{1}$$

where $\rho(\xi)$ is the charge density in the depletion region, and ε is the dielectric constant. This result may be more simply expressed by a one-dimensional integral using integration by parts, whereupon one obtains

$$V_s=-\int_0^w \frac{x\rho(x)}{\varepsilon} dx \ . \tag{2}$$

The depletion approximation assumes that the density of free carriers in the depletion region is negligible with respect to the charge at the local electron states. Therefore, the charge density in the depletion region may be expressed as

$$\rho(x)=-q\left[\sum_i f_i N_i(x)+\sum_j (1-f_j)N_j(x)\right] , \tag{3}$$

where the indices i and j denote acceptor and donor states, respectively; f_i (f_j) is the fractional population of the ith (jth) acceptor (donor) electron state, and $N_i(x)$ [$N_j(x)$] is its spatial distribution function. Obviously, the total charge in the space-charge region is given by

$$Q_b=\int_0^w dx\, \rho(x) \ . \tag{4}$$

This charge is neutralized by the total surface charge (Q_s). The width of the depletion region (w) is determined by the electrical neutrality requirement

$$Q_s=-Q_b \ . \tag{5}$$

Evidently, Q_s may also be described as a sum over all surface electron states, similar to the one in Eq. (3):

$$Q_s=q\left[\sum_i f_i^s N_i^s+\sum_j (1-f_j^s)N_j^s\right] , \tag{6}$$

where the index s denotes surface states and N^s is the surface-state density.

Illuminating the semiconductor may change the population of the local electron states, if the photons have sufficient energy to induce electron transitions from and/or to the local state. This population modification may induce a change in the width of the depletion region (Δw) and in the magnitude of the surface potential (ΔV_s). The latter is the essence of the SPS technique, since ΔV_s can be detected experimentally using the Kelvin probe method,[18] which measures the contact potential difference (CPD) between a vibrating reference probe and the semiconductor surface. It can easily be shown that the CPD is equal to the surface voltage to within an additive constant, which may be determined separately.[19] In most SPS investigations of local states, the depletion approximation is applicable even under external excitation. Therefore, all previous expressions (1)–(6) can be utilized in order to obtain the variation of V_s and Q_b in the form

$$\Delta V_s = V_s - V_s^0 = \frac{q}{\varepsilon}\left\{ \sum_i (f_i\chi_i - f_i^0\chi_i^0) + \sum_j [(1-f_j)\chi_j - (1-f_j^0)\chi_j^0] \right\}, \tag{7}$$

$$\begin{aligned} -\Delta Q_s = \Delta Q_b &= Q_b - Q_b^0 \\ &= -q\left\{ \sum_i (f_i\eta_i - f_i^0\eta_i^0) + \sum_j [(1-f_j)\eta_j - (1-f_j^0)\eta_j^0] \right\}, \end{aligned} \tag{8}$$

where the superscript 0 denotes thermal equilibrium values, and χ and η are the following functions of the width of the depletion region:

$$\chi_{i(j)} = \int_0^w dx\, x N_{i(j)}(x)\,, \tag{9a}$$

$$\eta_{i(j)} = \int_0^w dx\, N_{i(j)}(x)\,. \tag{9b}$$

It is worthwhile to note that ΔV_s depends only on the fractional populations f and f^s, because w may be expressed by them through Eqs. (4)–(6) and (7).

Let us now focus on the case where all bulk-state distributions $N(x)$ are spatially uniform. In this important case, analytical expressions for ΔV_s can be obtained: The integrals in Eqs. (9a) and (9b) may be calculated directly, and hence Eqs. (7) and (8) may be rewritten in the following form:

$$\Delta V_s = \frac{\rho w^2 - \rho_0 w_0^2}{2\varepsilon}\,, \tag{10}$$

$$-\Delta Q_s = \Delta Q_b = \rho w - \rho_0 w_0\,, \tag{11}$$

where ρ and ρ_0 are given by Eq. (3) for the case of uniform spatial distribution of bulk states, with and without illumination, respectively. The final expression for the variation of the surface potential is obtained by eliminating w and w_0 from Eq. (10) using Eq. (11) in the form

$$\Delta V_s = \frac{1}{2\varepsilon}\left[\frac{(\Delta Q_s + Q_s^0)^2}{\rho_0 + \Delta\rho} - \frac{(Q_s^0)^2}{\rho_0} \right], \tag{12}$$

where $\Delta\rho$ is the change in the density due to illumination

$$\Delta\rho = \rho - \rho_0\,. \tag{13}$$

Utilizing Eqs. (3) and (6), the variations of $\Delta\rho$ and ΔQ_s may be represented as linear combinations of the fractional populations

$$\Delta\rho = -q\left[\sum_i N_i \Delta f_i - \sum_j N_j \Delta f_j \right], \tag{14a}$$

$$\Delta Q_s = -q\left[\sum_i N_i^s \Delta f_i^s - \sum_j N_j^s \Delta f_j^s \right], \tag{14b}$$

where the variations of the fractional populations under external excitation are given for the surface and bulk states, respectively, by

$$\begin{aligned} \Delta f_{i(j)}^s &= f_{i(j)}^s - f_{i(j)}^{s0}\,, \\ \Delta f_{i(j)} &= f_{i(j)} - f_{i(j)}^0\,. \end{aligned} \tag{15}$$

So far, we have established the relation between the charge densities and the surface potential. However, if we are to understand how the surface potential is related to the illumination intensity, we must find the dependence of the population of the localized states on the illumination intensity. This relation is found by solving the time-dependent rate equation for the fractional population[6,13,16]

$$\frac{\partial f_{i(j)}}{\partial t} = g_p(1 - f_{i(j)}) - g_n f_{i(j)}\,, \tag{16}$$

where g_n and g_p are the generation rates for electrons and holes, respectively, and are given by

$$\begin{aligned} g_p &= e_p^{\mathrm{th}} + e_p^{\mathrm{opt}}\,, \\ g_n &= e_n^{\mathrm{th}} + e_n^{\mathrm{opt}}\,. \end{aligned} \tag{17}$$

Here, $e_n^{\mathrm{th}}, e_p^{\mathrm{th}}, e_n^{\mathrm{opt}}, e_p^{\mathrm{opt}}$ are the thermal and optical generation rates for electrons and holes, respectively. All carrier capture processes have been neglected due to the employment of the depletion approximation.

By definition, the optical generation rate is a product of the optical cross section $[\sigma_{n(p)}^{\mathrm{opt}}(h\nu)]$ and the illumination intensity $[I(h\nu,t)]$

$$e_{n(p)}^{\mathrm{opt}} = \sigma_{n(p)}^{\mathrm{opt}}(h\nu) I(h\nu,t)\,. \tag{18}$$

Under steady-state conditions, Eq. (16) has a simple solution

$$f_{i(j)} = \frac{g_p}{(g_p + g_n)}\,, \tag{19}$$

and the change in the fractional population with respect to its value in the dark can be easily shown to be

$$\Delta f_{i(j)}=\frac{(e_n^{\mathrm{th}}\sigma_p^{\mathrm{opt}}-e_p^{\mathrm{th}}\sigma_n^{\mathrm{opt}})I}{(e_p^{\mathrm{th}}+e_n^{\mathrm{th}})[e_p^{\mathrm{th}}+e_n^{\mathrm{th}}+(\sigma_p^{\mathrm{opt}}+\sigma_n^{\mathrm{opt}})I]} \ . \tag{20}$$

It is therefore understood that the illumination intensity controls the amount of excess charge [Eq. (20)], which in turn dictates the change in the surface potential [Eq. (12)].

III. SURFACE SENSITIVITY OF SPS

It has been previously argued[1,15] that the signal generated by the presence of bulk states may be significant enough to obscure the surface signal. Since the analysis of the previous section shows that bulk states may indeed contribute to the SPV signal, it is of importance to examine whether SPS is inherently a surface-sensitive technique. Alternatively, it may have been considered as one only because experimentally a change in the surface properties greatly affects the SPV.[5,8] We shall show that the former is correct by concentrating on the case of low illumination intensity, due to the ease of the mathematical treatment in this case. It is clear, however, that the conclusion is quite general. Also, in typical SPS experiments, the sample is illuminated through a monochromator, and the excitation is low enough to be considered as a perturbation.[13,16]

If the illumination intensity is low, the term containing I in the denominator of Eq. (20) may be neglected, and the relation between Δf and I reduces to a linear one:

$$\Delta f_{i(j)}=\frac{(e_n^{\mathrm{th}}\sigma_p^{\mathrm{opt}}-e_p^{\mathrm{th}}\sigma_n^{\mathrm{opt}})}{(e_p^{\mathrm{th}}+e_n^{\mathrm{th}})^2}I\equiv\beta_{i(j)}I \ , \tag{21}$$

where $\beta_{i(j)}$ is an illumination coupling coefficient. By inserting this relation in Eqs. (14) we obtain

$$\Delta\rho=-q\left[\sum_i N_i\beta_i-\sum_j N_j\beta_j\right]I \ , \tag{22a}$$

$$\Delta Q_s=-q\left[\sum_i N_i^s\beta_i^s-\sum_j N_j^s\beta_j^s\right]I \ . \tag{22b}$$

Also, using the assumption of low intensity illumination, one may obtain the change in the surface voltage and the surface charge upon illumination by applying calculus of variations to Eqs. (2) and (4), while paying attention to the fact that w may also be dependent on the illumination. The result is

$$\delta V_s=-\int_0^w\frac{x\,\delta\rho(x)}{\varepsilon}dx-\frac{\rho(w)}{\varepsilon}w\,\delta w \ , \tag{23}$$

$$\delta Q_s=-\int_0^w\delta\rho(x)dx-\rho(w)\delta w \ . \tag{24}$$

Combining Eqs. (23) and (24) we obtain

$$\delta V_s=\frac{w}{\varepsilon}\delta Q_s+\frac{w}{\varepsilon}\int_0^w\delta\rho(x)dx-\int_0^w\frac{x\,\delta\rho(x)}{\varepsilon}dx \ . \tag{25}$$

Writing $\delta\rho(x)$ as an explicit function of I, for the case of uniform spatial distribution of bulk states, we arrive at the final result:

$$\delta V_s=-q\left[\frac{w}{\varepsilon}\left[\sum_i\beta_i^sN_i^s-\sum_j\beta_j^sN_j^s\right]+\sum_i A_i\beta_i-\sum_j A_j\beta_j\right]I \ , \tag{26a}$$

where

$$A_{i(j)}=\int_0^w\left[\frac{w}{\varepsilon}-\frac{x}{\varepsilon}\right]N_{i(j)}dx \ . \tag{26b}$$

Equations (26) clearly indicate that for a sufficiently low illumination intensity, the change in the surface potential is proportional to the intensity. However, much more physical insight may be obtained from them. Equations (26) show that, in principle, all surface states and all bulk states within the depletion region contribute to the change in the surface potential. Each trap is characterized by two physical constants, $\beta_{i(j)}$ and $A_{i(j)}$. The term $\beta_{i(j)}$ contains only "interactive" physical information about the state, i.e., its emission coefficients, whereas $A_{i(j)}$ contains only "inherent" physical information about the state, i.e., its density and distance from the surface. Hence, we conclude that the proportionality constant between δV_s and I is a linear combination of the thermal and optical interactive properties of the states, and the weighting coefficients of this combination are determined by inherent properties (density and geometry) only.

Since the coefficients $A_{i(j)}$ decrease with the state distance from the surface, it follows that the deeper in the sample a state is located, the less it contributes to the change in V_s. This indicates that SPS is *inherently* more sensitive to surface than to bulk states. Thus, SPS merits its reputation as a surface-sensitive technique not only because local states are usually located at or near the surface, but also because the measurement technique is more sensitive to them. Nevertheless, it is obvious that bulk traps with sufficient density and/or a sufficiently high illumination coupling coefficient may generate a considerable signal. Therefore, in the next section we shall examine the difference in the response to surface and bulk states more closely, so that we may see whether or not they are distinguishable.

IV. CONTRIBUTION OF BULK VERSUS SURFACE STATES

Let us continue our investigation by returning to the final expression for ΔV_s, which does not assume low-level illumination [Eq. (12)]. We shall consider two limiting cases.

(1) The surface states are optically active, whereas the bulk states are inactive (or absent), i.e., the fractional population function of bulk states remains unchanged under excitation

$$\Delta f=0 \ \text{ and } \ \Delta\rho=0 \ . \tag{27}$$

In this case, the variation of the surface potential can be rewritten as

$$\Delta V_s = \frac{\Delta Q_s(\Delta Q_s + 2Q_s^0)}{2\varepsilon\rho_0} \ . \tag{28}$$

(2) The bulk states are optically active, and the surface states are optically inactive and have no communication with the bulk,[13] i.e.,

$$\Delta f_{i(j)}^s = 0 \ \text{ and } \ \Delta Q_s = 0 \ , \tag{29}$$

$$\Delta V_s = \frac{(Q_s^0)^2}{2\varepsilon\rho_0} \frac{(-\Delta\rho)}{(\rho_0 + \Delta\rho)} \ . \tag{30}$$

A comparison between Eqs. (28) and (30) leads to an unequivocal conclusion: under external illumination, identical optical activities of bulk and surface states ($N_i^s \Delta f_i^s \cong w N_i \Delta f_i$) *do not* lead to the same dependence between ΔV_s and Δf. Therefore, it is meaningful and of value to consider how these different relations may manifest themselves in an experiment.

As mentioned earlier, in typical SPS experiments, the excitation is low enough to be considered as a perturbation. In such a case, both Eqs. (28) and (30) give a similar linear relation between ΔV_s and Δf. For surface states,

$$\Delta V_s = \frac{Q_s^0}{\varepsilon\rho_0}\Delta Q_s \ \text{ or } \ \Delta V_s \propto \Delta f^s \ , \tag{31a}$$

for bulk states,

$$\Delta V_s = \frac{(Q_s^0)^2}{2\varepsilon\rho_0^2}(-\Delta\rho) \ \text{ or } \ \Delta V_s \propto \Delta f \ , \tag{31b}$$

and, therefore, the surface and bulk states are indistinguishable. This simple perturbation calculation readily explains why a difference in the behavior of surface and bulk states has never been experimentally observed before. To date, the only means of distinction between bulk and surface states has been observing the response of the SPV signal to different surface treatments.[3,17]

However, the $\Delta V_s(\Delta f)$ relations for surface and bulk states are significantly different when the illumination-induced charge is of the same order of magnitude as the total initial charge: For surface states,

$$\Delta V_s \propto \Delta f^s(\Delta f^s + 2f^{s0}) \ , \tag{32a}$$

for bulk states,

$$\Delta V_s \propto \frac{\Delta f}{1 + \dfrac{N_i}{\rho_0}\Delta f} \ , \tag{32b}$$

where in the first equation the presence of a single optically active surface state was assumed present, and in the second equation, a single optically active bulk state (with concentration N_i) was assumed.

Recently, it has been demonstrated that SPS experiments may be carried out using a tunable laser rather than a monochromator.[2] The use of laser radiation combined with appropriate optical attenuators provides a convenient means of obtaining a high illumination intensity, which is variable over may orders of magnitude. We shall now show that in this case, the surface and bulk states *are* distinguishable if we look more closely into the relation between Δf and the illumination parameters (photon energy and illumination intensity), which has been found in Eq. (20) and is restated here for convenience:

$$\Delta f_{i(j)} = \frac{(e_n^{\text{th}}\sigma_p^{\text{opt}} - e_p^{\text{th}}\sigma_n^{\text{opt}})I}{(e_p^{\text{th}} + e_n^{\text{th}})[e_p^{\text{th}} + e_n^{\text{th}} + (\sigma_p^{\text{opt}} + \sigma_n^{\text{opt}})I]} \ . \tag{33}$$

This relation is paramount for our present discussion, for it provides an insight into the distinction problem. It is evident that if the relation $\Delta f(h\nu)$ is to be utilized, then the optical cross sections $\sigma_{n(p)}^{\text{opt}}(h\nu)$ have to be known. However, these parameters are not well known: The theoretical determination of $\sigma_{n(p)}^{\text{opt}}(h\nu)$ is ambiguous due to the various possible sources of the electron states.[20–22] Experimental measurements of $\sigma_{n(p)}^{\text{opt}}(h\nu)$ are also unreliable since they involve assumptions about many other parameters. This unknown relation renders the use of the $\Delta V_s(h\nu)$ as a means of distinction between bulk and surface states impossible. However, the dependence of Δf on the illumination intensity is well defined by Eq. (33), and may be rewritten in a simplified form as

$$\Delta f_{i(j)} = \frac{d_1 I}{1 + d_2 I} \ . \tag{34}$$

Using Eq. (34), the previous expressions for ΔV_s, given by Eqs. (32), may also be written as simple functions of I. For surface states,

$$\Delta V_s \propto \left[\frac{d_1 I}{1 + d_2 I}\right]\left[\frac{d_1 I}{1 + d_2 I} + D\right] \ , \tag{35a}$$

for bulk states,

$$\Delta V_s \propto \frac{d_1 I}{1 + \left[d_2 + d_1 \dfrac{N_i}{\rho_0}\right] I} \ , \tag{35b}$$

where the definition of the symbolic constants d_1, d_2, and D is clear by inspection of the previous equations.

Equations (35) demonstrate the proper experimental tool for the distinction between bulk and surface states is the measurements of ΔV_s versus I, rather than the traditional ΔV_s versus $h\nu$ measurements. Careful inspection of Eqs. (35) show that the main feature of optically active surface states is that their corresponding $\Delta V_s(I)$ dependence may be superlinear, as in Eq. (35a). Bulk states, on the other hand, have a distinct sublinear $\Delta V_s(I)$, which asymptotically approaches a linear dependence for low enough illumination intensities. However, an experimentally measured linear or sublinear $\Delta V_s(I)$ relation is *not* sufficient to label a state as a bulk state, because such $\Delta V_s(I)$ dependence may also be obtained for surface states, depending on the values of the d parameters.

In order to examine the validity of the preceding analysis, which includes several simplifying assumptions (the most important of which is the depletion approximation) a comprehensive numerical model,[23] which does not incorporate such assumptions, has been adapted to the case of a free surface. A complete description of the physical and numerical aspects of this model is given in Ref. 23. The boundary condition at the free surface is the law of Gauss in a differential form:

$$\varepsilon_{\mathrm{sem}}\frac{\partial V}{\partial x}\bigg|_{\mathrm{sem}} - \varepsilon_{\mathrm{vac}}\frac{\partial V}{\partial x}\bigg|_{\mathrm{vac}} = Q_s \ , \tag{36}$$

where $\varepsilon_{\mathrm{sem}}$ and $\varepsilon_{\mathrm{vac}}$ denote the permittivity in the semiconductor and the vacuum, respectively, and Q_s is the interface charge.[24]

In the numerical simulations, an n-type semiconductor substrate ($N_d = 5\times10^{17}$ cm^{-3}) with the bulk properties of GaAs, is illuminated by monochromatic light at a wavelength of 1200 nm and with an intensity which is varied over a wide range of 10^6 photon cm^{-2} s^{-1} to 10^{17} photon cm^{-2} s^{-1}. As an example, we consider a substrate that includes bulk and surface-acceptor states with the same parameters: $E_t = E_c - 1$ eV, $\sigma_n = 10^{-20}$ cm^{-2}, and $\sigma_p = 10^{-18}$ cm^{-2}. The simulations were carried out in the two limiting cases: either the bulk or the surface state is optically inactive. The optical cross sections are $\sigma_n^{\mathrm{opt}} = 10^{-17}$ cm^{-2} and $\sigma_p^{\mathrm{opt}} = 2\times10^{-17}$ cm^{-2} for the active state, and zero for the passive one. The bulk-state density is 10^{17} cm^{-3}, and the surface-state density is 2×10^{12} cm^{-2}.

The calculated $\Delta V_s(I)$ relations are illustrated in Fig. 1. The results of the analytical expressions are also shown. The absolute magnitude of ΔV_s was about three times greater when the surface state was optically active and reached a value of 150 mV. In this case, the simple depletion-approximation expression for ΔV_s [Eq. (35a)] is in excellent agreement with the results of the simulation. In the second case, there is a significant disagreement between the calculated data and Eq. (35b). Instead of the saturation region, the numerical results display a finite slope—a "soft" saturation. This deviation from the analytical theory in the case of bulk states is obtained because bulk states exhibit a spatial distribution of their occupation. For example, the distribution of the free electrons changes significantly near the edge of the depletion region, and therefore the fractional population of the bulk states is not uniform. Moreover, outside of the depletion region, carrier capture processes play a dominant role in the determination of the population of the local electron states, while they are negligible within the depletion region. Therefore, under illumination, the fractional population obtains its steady-state value at different light intensities inside and outside of the depletion region. The variation of the depletion-region width under illumination changes the balance between states inside and outside the depletion region, thereby causing the soft-saturation effect. Evidently, in this case the depletion approximation is no longer valid in the high-intensity regime. In contrast with bulk states, all surface states are equidistant from the edge of the depletion region, and the depletion approximation holds because the states are far away from it. Therefore, the presence of a soft-saturation region is characteristic of bulk states.

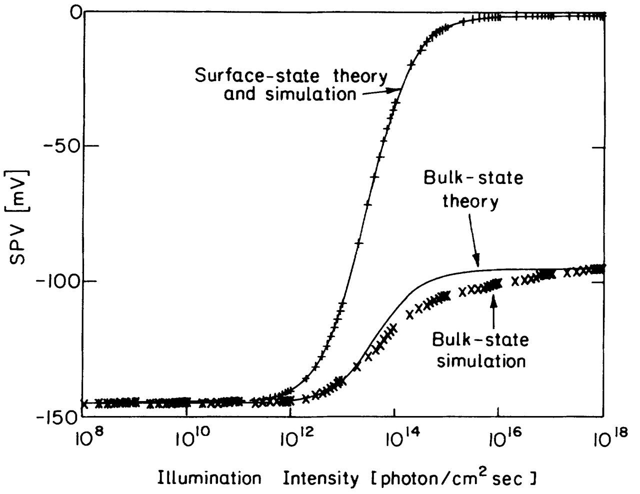

FIG. 1. Dependence of the surface photovoltage on the illumination intensity: Numerical simulation and analytical results for a surface state and a bulk state.

V. EXPERIMENTAL RESULTS

Having described and proved the general concepts behind our scheme for distinction between surface and bulk traps, it is the purpose of this section to show the results of experiments conducted on InP samples. The discussion of these experiments may serve as a practical guide of steps to be taken and pitfalls to be avoided when using our proposed approach.

All surface-photovoltage experiments were performed in air using a Kelvin probe for the CPD measurements. The Kelvin probe (Delta-Phi Elektronik, Germany) consisted of a semitransparent 2.5-mm-diam Au grid, and has been described in detail elsewhere.[5] A Ti:sapphire tunable laser (Model 890, Coherent, USA, pumped by a 5-W argon-ion laser) was used as a high-intensity light source, and a grating monochromator (Oriel, USA) was used as a low-intensity light source. The illumination intensity was varied by means of adjustable neutral-density filters.

We performed intensity-resolved SPS experiments as described in the previous section on two types of InP bulk material: The first sample was a semi-insulating ($\rho \sim 10^8\ \Omega$ cm) InP(100) wafer. It is well known that semi-insulating InP is usually compensated by deep impurities,[25] so a large bulk signal was expected for such samples. The second sample studied was a device grade 5×10^{16} cm^{-3} p-type InP(100) wafer. A device-grade doped wafer should ensure the absence of a sizable density of bulk states. In order to obtain a high density of surface states, an extremely small amount of In was evaporated on the InP substrate at an oxygen pressure of 5×10^{-4} torr. Such evaporation may indeed be considered as causing a perturbation to the surface, rather than creating a film of new material on top of the InP substrate.[26,27]

Figure 2 shows the SPV as a function of the illumination intensity, at an illumination wavelength of $\lambda \cong 942$

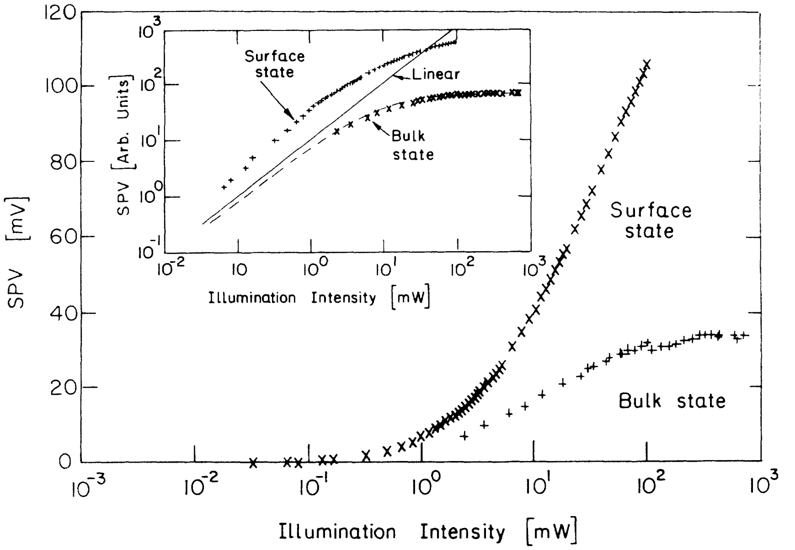

FIG. 2. Dependence of the surface photovoltage on the illumination intensity for InP samples. +, doped sample; ×, semi-insulating sample. Inset: Logarithmic plot of the same SPV (I) dependence in arbitrary units. Curve represents fitting according to Eq. (35b).

nm for the semi-insulating sample, and of $\lambda \cong 1005$ nm for the doped sample. By comparison to Fig. 1, it can be clearly seen that the experimental results are in very good agreement with the theoretical predictions based on the analytical theory and the numerical simulation. For the semi-insulating sample, the measurement results fit Eq. (35b) very closely, up to saturation intensities, with $d_2+d_1N_i/\rho_0 \cong 0.12$. A soft-saturation regime is also visible. In the SPV versus I curve for the doped sample, a distinctly superlinear region can be observed. This can be verified by means of the logarithmic plot, which is inset in the figure. As explained above, this establishes the presence of surface states unequivocally.

It is most important to notice that most of the doped-sample SPV versus I graph is sublinear, so that a sublinear dependence must be considered as inconclusive, unless a fit with Eq. (35b) has been obtained, or a soft-saturation region has been observed. Also, the superlinearity observed, although distinct, is quite small. It should be noted that a large superlinearity is not to be expected. Inspection of Eq. (35a) reveals that a superlinear dependence may only be found for relatively small light intensities, because for higher intensities, the denominator dominates and the relation is sublinear. For such intensities, the change of electron population Δf is relatively small. Inspection of Eq. (32a), on the other hand, reveals that a significant superlinear dependence will only be observed if Δf is of the same order of the initial population f_0 and this is unlikely to happen at low illumination intensities.

Unfortunately, the nature of the saturation in the case of the doped sample cannot be assessed in this experiment, due to insufficient laser power. Nevertheless, the curves of Fig. 2 closely resemble the simulation results of Fig. 1, and it is reasonable to assume they follow suit at higher intensities too.

The results presented also serve as a guide to the general experimental procedure to be taken for the distinction between surface and bulk states: A soft-saturation regime is characteristic of bulk states, and a superlinear SPV versus I graph is characteristic of surface states. Therefore, experimental observation of either feature serves as direct evidence for the types of traps involved. Nevertheless, surface states do not have to have a superlinear SPV versus I dependence, and the precise type of saturation may remain undetermined due to insufficient laser power, as in this experiment. In such cases, a fitting to Eqs. (35) should be attempted. Another complication that should be taken into consideration is the possible presence of a non-negligible concentration of both surface and bulk traps. In such a case, it is straightforward to construct expressions analogous to Eqs. (35) and attempt to fit them to the experimental results. Also, if several traps are present, their energy positions are most easily resolved by regular SPS.[3] Then, intensity-resolved experiments, as described here, may be undertaken at different wavelengths, which may only excite electrons (or holes) in some of the traps. Thus, the contribution of each type of trap may be independently assessed.

VI. CONCLUSIONS

In conclusion, we have carried out a theoretical analysis which shows that SPS is inherently more sensitive to surface states than to bulk states. Moreover, we have shown that examination of the relation between V_s and I shows a way to distinguish between bulk and surface states by means of SPS experiments. Under the depletion approximation, analytical expressions for ΔV_s were obtained in two limiting cases, where either the surface or bulk states are optically inactive. When the surface states are optically active, the results of a numerical simulation are in an excellent agreement with the predictions of the simple analytical formula. In the opposite case, the increase of ΔV_s with illumination intensity is significantly slower than that predicted by the simple theory. Thus, the distinction of surface and bulk states may be carried out using intensity-resolved SPS. A soft-saturation regime is characteristic of bulk states, and a superlinear $\Delta V_s(I)$ is characteristic of surface states. These conclusions have been supported by experiments on two samples of InP: one with a high density of bulk states and the other with a high density of surface states.

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[1] H. C. Gatos and J. Lagowski, J. Vac. Sci. Technol. **10**, 130 (1973).

[2] L. Kronik, L. Burstein, Y. Shapira, and M. Oron, Appl. Phys. Lett. **63**, 60 (1993).

[3] L. Burstein and Y. Shapira, Semicond. Sci. Technol. **8**, 1724 (1993).

[4] J. Szuber, Appl. Surf. Sci. **55**, 143 (1992).

[5] L. Burstein, J. Bregman, and Y. Shapira, J. Appl. Phys. **69**, 2312 (1991).

[6] L. Kronik and Y. Shapira, J. Vac. Sci. Technol. A **11**, 3081 (1993).

[7] S. Kuzminski, K. Pater, and A. T. Szaynok, Surf. Sci. **247**, 90 (1991).

[8] Y. Rosenwaks, L. Burstein, Y. Shapira, and D. Huppert, Appl. Phys. Lett. **57**, 458 (1990).

[9] A. L. Musatov, S. V. Geizer, and A. D. Korinfskii, Fiz. Tekh. Poluprovodn. **23**, 2056 (1989) [Sov. Phys. Semicond. **23**, 1271 (1989)].

[10] J. L. Shaw, R. E. Viturro, L. J. Brillson, D. Kilday, and G. Margaritondo, J. Electron. Mater. **17**, 149 (1988).

[11] L. J. Brillson, Appl. Surf. Sci. **22-23**, 948 (1985), and references therein.

[12] H. Fritzsche, Semicond. Semimet. **21**, 309 (1984).

[13] C. L. Balestra, J. Lagowski, and H. C. Gatos, Surf. Sci. **64**, 457 (1977).

[14] J. R. Maltby, C. E. Reed, and C. G. Scott, Surf. Sci. **51**, 89 (1975).

[15] K. G. Germanova, L. L. Constantinov, and V. L. Strashilov, Surf. Sci. **128**, 447 (1983).

[16] L. Szaro, Phys. Status Solidi A **113**, 97 (1989).

[17] I. A. Davydov, L. P. Strakhov, and S. L. Tselishchev, Fiz. Tekh. Poluprovodn. **26**, 159 (1992) [Sov. Phys. Semicond. **26**, 89 (1992)].

[18] W. Thomson (Lord Kelvin), Philos. Mag. **5**, 46 (1898).

[19] L. J. Brillson, Surf. Sci. Rep. **2**, 123 (1982).

[20] A. L. Musatov and S. V. Geizer, Fiz. Tverd Tela (Leningrad) **33**, 124 (1991) [Sov. Phys. Solid State **33**, 69 (1991)].

[21] H. G. Grimmeiss and L-Å. Ledebo, J. Phys. C **8**, 2615 (1975).

[22] G. Lucovsky, Solid State Commun. **3**, 299 (1965).

[23] G. Ashkinazi, M. Leibovitch, and M. Nathan, IEEE Trans. Electron Devices **40**, 285 (1993).

[24] S. Seberhorr, *Analysis and Simulation of Semiconductor Devices* (Springer-Verlag, New York, 1984).

[25] J. P. Fillard, in *Properties of InP,* edited by S. Adachi and J. Brice (Inspec, London, 1991), p. 249.

[26] V. Korobov, Y. Shapira, B. Ber, K. Faleev, and D. Zushinskiy, J. Appl. Phys. **75**, 2264 (1994).

[27] A. Golan, Y. Shapira, and M. Eizenberg, J. Vac. Sci. Technol. B **11**, 567 (1993).