

Reply to J. Hlavka's Comment on "Role of photocurrent in low temperature photoemission studies of Schottky-barrier formation."

**Michael H. Hecht
Center for Space Microelectronics Technology
Jet Propulsion Laboratory, California Institute of Technology**

Dr. Hlavka addresses three aspects of the treatment of temperature dependent photovoltage effects in photoemission spectroscopy of Schottky barrier formation which were first published in references 1 and 2. He points out certain discrepancies in the analytical derivation; he argues that the "proper" band picture should incorporate the concept of quasi Fermi levels (QFL); and he questions the validity of the calculation in light of microscopic effects such as temperature-dependent interface state distributions and recombination velocities. In the following, I show that the differences in derivation are largely a matter of nomenclature, that the equilibrium band diagram is the correct one for the photoemission experiment, and that the details of charge trapping do not significantly compromise the calculation. Dr. Hlavka's conclusion that "photoelectron measurements made at different temperatures cannot be simply correlated" belies the evidence that this simple model has proven remarkably successful at predicting and explaining measured results on a wide variety of systems.

1. My derivation closely followed that of Rhoderick and Williams (RW).³ The critical equations correspond to 3.27 and 3.27a in RW with two exceptions. One is an unfortunate change in nomenclature, as my V_d corresponds to RH's $(V_d + \xi)$. In the RH version, V_d refers, logically, to the diffusion potential, whereas in my work it refers to the "observed" barrier height relative to the spectrometer Fermi level. Secondly, in my equation (3), I explicitly define the actual diffusion potential in terms of the depletion width w in order to remove the dependence on x-ray absorption depth a for the case where $aw < 1$. This is described in a footnote.

Dr. Hlavka's comments that my V_d should actually be the barrier height V_b and that the sign of the voltage in the term $(1 - e^{-qV_d/kT})$ is incorrect, is easily explained in terms of a subtle (and insignificant) difference between the RH derivation and the earlier forms cited by Dr. Hlavka. With V defined as positive for forward bias, equation (1) was originally written:

$$(1) \quad J_{pc} = J_0(T) e^{-qV_d/kT} (1 - e^{-qV_d/kT})$$

Dr. Hlavka suggests instead:

$$(2) \quad J_{pc} = J_0(T) e^{-qV_b/kT} (1 - e^{+qV/kT})$$

Consider the case where the ideality factor is unity (i.e. $qE_0 = kT$). Since $V_b = V_d + V$, the two equations are then equivalent (except for the arbitrarily chosen sign of the photocurrent). The slightly different application of the ideality factor is described in RH (p. 99) as a correction to the earlier works which neglected the fact that "barrier lowering affects the flow of electrons from metal to semiconductor as well as the flow from semiconductor to metal."

In practice, the simplifications in references 1 and 2 were primarily introduced for pedagogical reasons (see item 3 below). The actual calculations used a complete methodology including explicit computation of the exponentials and the use of empirical temperature dependent values for the band gap and Fermi level positions.

2. The "proposed" band diagram is, indeed, the correct one to describe a photoelectron spectroscopy (PES) experiment. In PES, the peak positions are determined relative to the spectrometer Fermi level which, in turn, is in equilibrium with the bulk of the sample. PES samples a region very close to the surface. In all but degenerate semiconductors, in fact, the measurement depth is so much smaller than the depletion width that no measurable peak broadening is observed. Under illumination, a charged capacitor is effectively placed between the spectrometer ground and the sampled region. One side of this capacitor is the sheet of charge on the metal, while the other side is the charge dispersed through the depletion region. The potential varies continuously across this region, but the total offset seen by the spectrometer is determined by the charge and the capacitance according to $V=Q/C$.

Dr. Hlavka's "realistic" model may be a more appropriate way to represent the *energetic* distribution of electrons in the conduction band. The "proposed" model of reference 1, however, describes the *spatial* distribution of charge and the spatial variation of electrical potential to which the PES measurement is sensitive. The quantities represented in this picture are well defined in the depletion region. The Fermi level is that of the bulk sample, and is defined to be flat. The band positions vary relative to that level in proportion to the integrated net charge between the bulk of the semiconductor and the point in question. The positions are insensitive to whether that charge consists of minority or majority carriers or whether it is at the Fermi level or excited above it. This is the relevant definition for this measurement because, in PES, the band positions are inferred from the energy required to remove electrons from below the Fermi level into the vacuum.

There is interesting anecdotal evidence supporting this point of view. A specific prediction of my "proposed" model is that the energy *difference* between PES peaks from the metal and the semiconductor will be insensitive to the photovoltage. Unfortunately, previous researchers only measured the semiconductor-derived peak energies relative to their bulk values. The corresponding energy shift in the metal-derived peaks had been noted by some authors, but was incorrectly attributed to the transition from dispersed metal atoms to a bulk metal environment. In contrast, PES studies of band offset evolution in semiconductor heterostructure formation typically focused on the difference between peaks derived from the semiconductors on each side of the junction. These authors thereby avoided errors due to x-ray induced charging effects.

3. Dr. Hlavka is correct in pointing out the complexity of the photovoltaic process from a microscopic point of view. The difficulty of exact calculation, in my opinion, is the reason the photovoltage phenomenon was overlooked in this context for so long. The details of trapping, recombination, and other heterogeneities of the depletion region are, in fact, overshadowed by far greater uncertainties in the estimate of the photocurrent. Typically the incident photon flux is not well known, nor is the reflectivity of the surface, nor the quantum

efficiency of electron-hole pair generation from x-rays. The doping is also typically not known with sufficient accuracy to quantitatively determine the depletion width.

The success of my approach to this problem is due to the modeling of the Schottky barrier as a simple circuit element. The reason this works so well is revealed by equation (2) of reference 1. For photovoltages of any significant magnitude, the measured band position is given by:

$$(3) \quad V_d = E_0 \ln(J_0/J_{pc})$$

where E_0 , for the low temperatures of greatest interest, is on the order of 10 mV. As a result, even an order of magnitude error in the estimation of J_{pc} or J_0 , which might result from the above sources, will introduce only tens of mV error in the calculated voltage.

Although the calculated value of V_d is insensitive to the types of phenomena Dr. Hlavka describes, it is extremely sensitive to temperature. Measurement of sample temperature in vacuum is an inexact art, and most of the differences between measured and calculated photovoltages can be attributed to small, systematic errors in temperature measurement. In addition, as described in reference 2, the principal competing effect is leakage resistance (which may also be modeled as a circuit element). In short, the approximations in this formalism introduce errors which are substantially smaller than the uncertainties in the measurement itself.

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¹M. H. Hecht, Phys. Rev. B41, p. 7918, 1990.

²M. H. Hecht, J. Vac. Sci. Technol. B8, p. 1018, 1990

³E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts*, 2nd edition, Clarendon Press, Oxford, 1988.