Effect of Van Hove singularities on the photovoltage spectra of semiconductors

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The role of band structure in the photovoltaic effect is examined. Photovoltage is predicted to be sensitive to Van Hove singularities. This prediction is verified experimentally. Spectra of GaAs, GaP, and GaN at above-band-gap photon energies are compared with calculated band structure showing that band features, such as conduction band valleys and valence band peaks, have a clear manifestation in photovoltage spectra, for both direct and indirect transitions. This effect facilitates a band structure probe. This probe reveals experimental evidence on the $2H$-GaN valence band structure.

I. INTRODUCTION

Illumination can induce transitions between electronic states in matter. In the presence of an *external* electric field, photoexcited electrons may be emitted from matter, i.e., photoemission.[1] In the presence of an *internal* electric field, e.g., a space-charge region in semiconductors, the excited carriers are swept and separated giving rise to surface charging, also known as the photovoltaic effect.[2,3] Both photoemission and the photovoltaic effect have provided the basis for electronic state spectroscopies. While methods based on photoemission, e.g., x-ray photoelectron spectroscopy, require ultrahigh vacuum conditions, photovoltaic methods may conveniently be carried out in air. Photoemission methods typically employ excitation at photon energies exceeding the forbidden gap of most semiconductors, i.e., *above-band-gap* illumination, and often suffer from parasitic photovoltage.[4] On the other hand, the photovoltaic effect has found significant use as a deep-level spectroscopy using *below-band-gap* illumination.[5–8]

In this paper, manifestations of Van Hove singularities[9] in photovoltage spectra are predicted theoretically and verified experimentally using above-band-gap illumination. A Van Hove singularity is a local increase in the density of states (DOS) associated with a band structure feature at which

$$\nabla E(k) = 0, \tag{1}$$

where E is the energy and k is the wave vector.[9,10] Due to the increased density of states associated with these band features, optical transitions are more likely to originate at a singularity of a filled band (e.g., valence band peaks) and end up at a singularity of an empty band (e.g., conduction band valley).[11] To date, above-band-gap photovoltage has been used to measure diffusion length.[12] As will be discussed further on, photovoltage depends on several material properties, including the absorption of light. The increased absorption often associated with certain band features has led to the use of photovoltage to measure band gaps.[13,14] As we show here, absorption alone can only account for a limited part of the picture. The physical model and experimental results presented herein suggest that band features have a role in the photovoltaic effect and that above-band-gap photovoltage can provide valuable band structure information as well.

II. MODEL AND PREDICTION

Above-band-gap illumination excites both deep levels and electron-hole pairs. If the photon wavelength scan starts at below-gap energies, the deep levels are already excited before the band edge energy is reached. As the band edge is approached, two opposing trends come into effect. One is the excitation of electrons from the valence band into the conduction band, generating pairs of electrons and holes. The other is a decrease of the absorption depth α^{-1}. The result of the latter is a decrease of the photoexcited volume, which allows relaxation of deep levels at the deep parts of the sample. This relaxation is a continuous process, because as the photon energy increases less and less bulk is illuminated. This trend is perturbed by electron-hole pair-generation-related photovoltage, which is at the focus of our interest.

Electron-hole pair generation takes place near the surface, within the photon absorption depth. It sets in slightly below the band edge due to the Franz-Keldysh effect.[15] The photogenerated pairs are separated by the built-in field commonly present at semiconductor surfaces, typically resulting in a positive (negative) photovoltage in the case of an *n*-type (*p*-type) semiconductor.[16] The same photogeneration also results in carrier concentration gradients working to diffuse the excess carriers into the bulk. Since electron mobility is always higher than that of holes, electrons diffuse faster giving rise to a positive photovoltage, in a process known as the *Dember effect*.[17,18] Hence, above-band-gap photovoltage may still result from electron-hole generation at the surface even in the absence of a built-in field, what makes it less sensitive to surface conditions. The processes of photoexcitation and charge separation are schematically illustrated for the case of an *n*-type semiconductor in Fig. 1.

In direct gap semiconductors, generation of electron-hole pairs at the band edge energy is typically manifested in a strong steplike photovoltage transition, reflecting a step in the absorption coefficient. Electrons in the valence band outnumber those in deep levels by orders of magnitude. Hence, the probability of exciting an electron from the valence band is higher than that from deep levels resulting in a relatively intense transition. Indirect transitions also require phonons, reducing the transition probability and thereby its intensity.

The above-band-gap photovoltage has been the subject for theoretical treatments, because of the interest in it as a
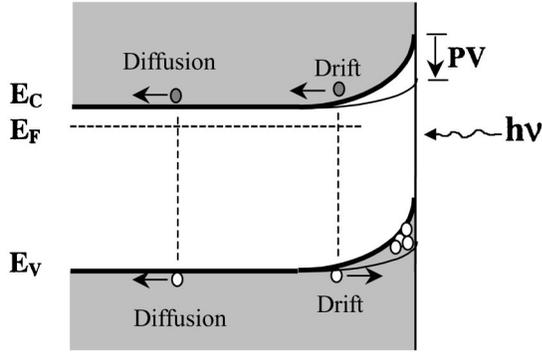
FIG. 1. The main above-band-gap photoexcitation processes shown schematically on a band diagram of a depleted surface of an *n*-type semiconductor.

minority-carrier diffusion-length probe. In its most general form, formulated by Liu *et al.*, the photovoltage magnitude *PV* can be expressed as[19]

$$PV(h\nu) = \Phi[1 - R(h\nu)]f(\alpha, L) \quad (2)$$

where $h\nu$ is the photon energy, Φ is the photon flux, R is the reflectance, L is the minority carrier diffusion length, and $f(\alpha, L)$ takes the form[19]

$$f(\alpha, L)$$

$$= \frac{f_1(\alpha, L)\exp(-\alpha w) + C_1[1 - \exp(-\alpha w)] - C_2\alpha/w}{C_3 + C_4 D/L + C_5 w D/L^2}$$

$$(3)$$

where w is the width of the surface depletion region under the depletion approximation, D is the minority-carrier diffusion coefficient, C_1, C_2, C_3, C_4, and C_5 are sample-specific terms that do not vary with the photon energy, and[19]

$$f_1(\alpha, L) = \frac{S}{S + D/L}\frac{\alpha L}{1 + \alpha L} \quad (4)$$

where S is the surface recombination velocity in a Shockley-Read-Hall type of recombination center. Based on Eqs. (2)–(4), one can predict that the photovoltage will be sensitive to Van Hove singularities through three parameters. One is the absorption coefficient, reflecting the DOS, which sometimes changes abruptly at Van Hove singularities. The second is the minority-carrier diffusion length L, which differs from one conduction band valley to another and from one valence band peak to another due to the different carrier lifetimes at different energies. The third, the optical reflection R, a band structure probe in its own right, takes place at the surface affecting the amount of absorbed light as a function of photon energy. Each of these parameters senses band structure features and contributes to the photovoltage. However, above the band edge, the optical reflection has a rather weak effect on photovoltage,[20] while the absorption coefficient typically shows a gradual featureless increase (except for the case of an indirect semiconductor where both may still show a definite feature at the first direct gap).[21] This leaves L as the main sensor.

Indeed, it is occasionally observed that PV vs α^{-1} curves, employed in evaluation of L, deviate from linearity away from the fundamental band gap.[22] In negative electron affinity photoemission yield vs α^{-1} curves, such deviations were related to excitation to upper conduction band valleys and were used to calculate L therein.[23] The sensitivity to L implies that *n*-type material should be more sensitive to valence band peaks, while *p*-type material should be more sensitive to conduction band valleys.[24] This sensitivity should make the photovoltage a good sensor of band features. Hereafter, we test this hypothesis experimentally using three III-V semiconductors. The generality of the model is not limited by this material selection.

III. EXPERIMENTAL DETAILS

To measure changes in the surface voltage, we used a Kelvin probe in a dark Faraday cage with the same setup commonly used for surface photovoltage spectroscopy.[7,25] Note that by choosing this method we do not limit the generality of our conclusions, as the same effect should be expected with any other form of the photovoltaic effect. The samples were illuminated using a monochromatized and filtered quartz-tungsten-halogen source operated in a constant photon flux regime. For the GaN samples, a Xe lamp was used and the results were intensity normalized after verifying a linear intensity dependence of the photovoltage. The photon flux was $\sim 10^{12}$ photons cm^{-2} s^{-1}. The results are given in the form of the contact potential difference (CPD). The photovoltage is defined as the difference between the dark CPD and the CPD under illumination.

The GaAs samples were cut from a wafer (MCP Inc., U.K.) *n*-type doped with 6×10^{16} Si/cm^3. The GaP samples were cut from a wafer (Elma Inc., U.S.A.) *p*-type doped 5×10^{17} Zn/cm^3. The GaN samples were 2 μm thick epilayers unintentionally doped (*n* type) to 4×10^{17} cm^{-3} grown on sapphire.[26] The GaAs and GaP samples were grounded using back Ohmic contacts. The GaN epilayers were contacted from the front (details were given elsewhere).[25] All the measurements were carried out in *air* at *room temperature* on the free surfaces of the samples without any special preparation.[27]

IV. RESULTS AND DISCUSSION

Figure 2 shows the CPD measured on the surface of a typical *n*-type GaAs sample. A sharp CPD decrease is observed as the photon energy approaches the GaAs band edge energy. This transition is denoted with arrow 1 also in the band structure scheme shown in the inset (after Chelikowsky and Cohen[28]). The direction of this transition agrees with the *n*-type conductivity of the sample.[29] A more moderate decrease in the CPD follows this point, which can be explained by the interplay between the increase of the DOS, as states deeper in the conduction and valence bands are made available by the increasing photon energies, and the relaxation of deep levels as the absorption depth decreases. At $\sim$1.7 eV, the CPD changes from negative to positive slope (arrow 2). This point corresponds clearly with the next conduction band
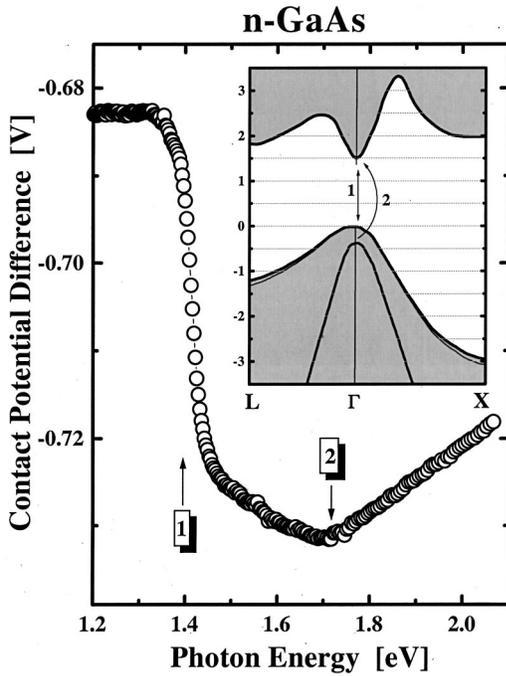
FIG. 2. Contact potential difference spectrum obtained from the free surface of *n*-type GaAs(100). The inset shows the band structure of GaAs [after Chelikowsky and Cohen (Ref. 28)].

valley at the *L* symmetry point of the first Brillouin zone of GaAs. At this point, $\nabla E(k)=0$ and one could expect an increase in the DOS. A DOS increase should further decrease the CPD. Instead, we observe an increase. Why?

A conduction band valley carries majority carriers. The photovoltage is not sensitive to the lifetime of majority carriers.[10] Therefore, the only way for the *L* valley to affect the photovoltage is through the absorption coefficient. Examining the absorption spectra of GaAs, we find no evidence for the *L* valley or the *X* valley.[30] This is further supported by the calculated DOS, where no features are observed at either of these symmetry points.[31] Thus, there seems to be no obvious reason for the GaAs *L* or *X* valley to affect the photovoltage in *n*-type GaAs. Indeed, no slope change is observed at the *X*-valley-related photon energy. We therefore look for a valence band feature. Indeed, the *spin split-off* valence band is known to be located 0.34 eV below the valence band maximum. This is somewhat higher than the observed threshold. However, the Franz-Keldysh effect is expected to redshift the direct transitions, as is commonly observed at the fundamental band edge of direct semiconductors and is also observed in our measurement.

Since this valence band is not apparent in absorption or reflection spectra, the only way it can affect the photovoltage is through a change in the minority-carrier diffusion length, compared with the one at the valence band maximum. The observed photovoltage decrease may be accounted for by a decrease in *L*. The change in *L* is not abrupt, because only a fraction of the carriers is expected to form at the lower peak while the rest are still formed at the Γ peak. This fraction increases gradually with the photon energy,[23] in agreement with the observed gradual photovoltage decrease (CPD in-
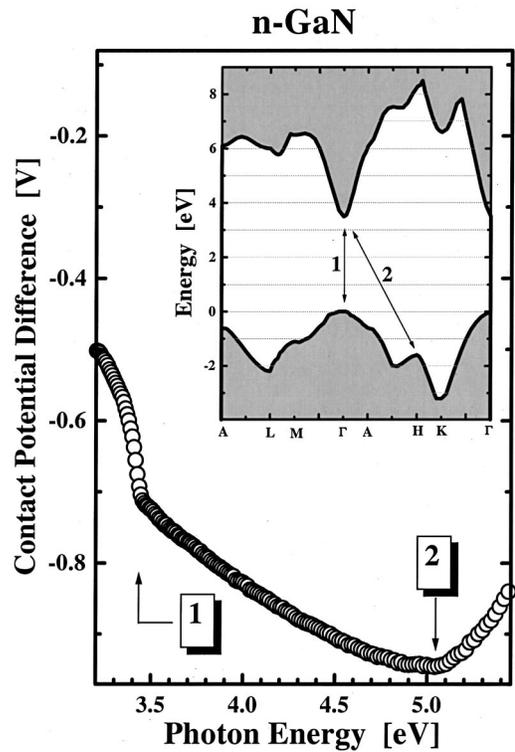
FIG. 3. Contact potential difference spectrum obtained from the free surface of *n*-type GaN film grown on sapphire. The inset shows the band structure of GaN [after Rubio *et al.* (Ref. 35)].

crease). Hence, we conclude that the observed transition, setting in at ~1.7 eV, expresses the influence of the GaAs split-off valence band.

Figure 3 shows a photovoltage spectrum obtained from a typical GaN sample. As all the conduction band features other than the Γ valley are well beyond the range of our measurement, we can safely infer that all the observed transitions target the lowest valley at the GaN Γ symmetry point. The first one, observed at ~3.4 eV (denoted 1), clearly relates to a direct Γ-to-Γ transition from the highest valence band peak to the lowest conduction band valley, in agreement with the fundamental energy gap of the 2*H* polytype of GaN. The next clear transition, observed at 5.1 eV, seems to relate to the next valence band peak at the *H* symmetry point. This transition causes a decrease of the photovoltage, suggesting that the hole diffusion length in the *H* peak is smaller than that in the upper valence band peak at Γ. This result presents experimental evidence for the Γ-*H* energy spacing in the 2*H*-GaN valence band.

To present a more complete set of evidence, we examined spectra of *p*-type GaP. Unlike GaAs and GaN, GaP presents a case of an indirect band gap. As already observed in the previously presented cases of GaAs and GaN, indirect transitions are inherently weaker than direct ones. The spectrum of a typical GaP sample, shown in Fig. 4, contains some below-band-gap transitions involving deep levels, which are not within the interest of the current study. Below-band-gap transitions are direct transitions. Therefore, it is not surprising that the indirect band edge transition that follows slightly below the fundamental gap (~2.26 eV) is relatively weak
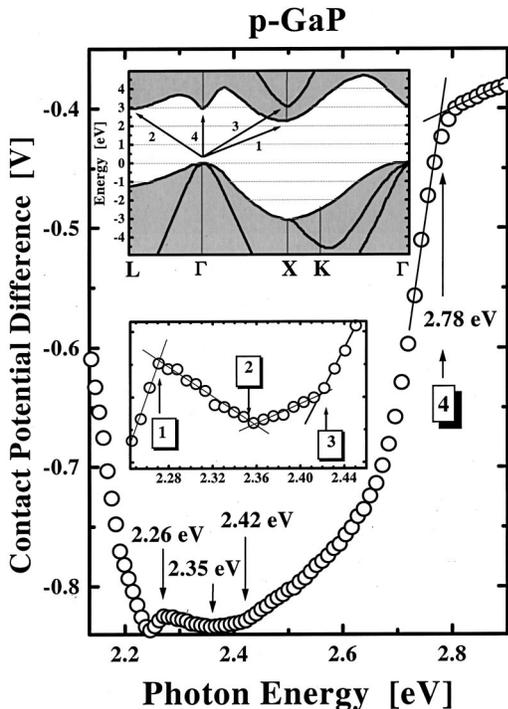
FIG. 4. Contact potential difference spectrum obtained from the free surface of p-type GaP. The inset shows the band structure of GaP [after Chelikowsky and Cohen (Ref. 28)].

and only perturbs the deep-level one. This transition is from the highest conduction band peak at the Γ symmetry point to the conduction band valley at the X point (denoted transition 1). The next transition at the L point is indirect and weak as well (transition 2 at 2.35 eV). The third transition, at 2.42 eV, corresponds to the next conduction band at the X point. Finally, the strong steplike transition setting in at 2.66 eV and leveling off at 2.78 eV is the first direct gap transition at the Γ point, and is indeed strong as expected. All the transitions show the effect of a reduction in the electron diffusion length associated with the valleys at the L and X points.

As a band structure probe, photovoltage presents several advantages. First, some of the common band structure probes, e.g., electroreflectance and photoreflectance, are based on modulation, which is the electronic means for derivation.[32] Above-band-gap photovoltage spectra provide good signal to noise without any form of derivation. Second, it may also sense strong photoreflectance features. Third, it cannot be perturbed by parasitic photovoltage as is x-ray

photoelectron spectroscopy. Finally, unlike the case of below-band-gap photovoltage spectroscopy, used to characterize deep levels and surface states, above-band-gap photovoltage is not sensitive to surface preparation (which may affect the initial surface charge). The Dember effect makes it possible to detect band features by photovoltage even in the absence of an initial surface charge.[17]

Above-band-gap photovoltage requires p-type material to sense conduction band features and n-type material to sense valence band features. This may find use as a complementary method to ballistic electron emission spectroscopy, where n-type material is used to study the conduction band and p-type material is used for the valence band.[33,34] In cases of new materials, in which control over the doping has not been fully achieved, it is sometime desired to use the unintentional form of conduction. For example, wurtzite GaN is unintentionally doped n type, while p type is often obtained through heavy compensation doping which may distort some of the material properties. Other examples are zinc blende GaN, which is unintentionally p type, and ZnO that is unintentionally n type.

V. CONCLUSION

The spectra presented here form a consistent set of evidence showing that photovoltage manifests conduction band valleys and valence band peaks via its sensitivity to minority-carrier lifetime and DOS, as we predicted. The observed band features should also be reflected in deep-level spectra, especially in minority-carrier transitions. In addition to the energy offsets, photovoltage spectra may hold quantitative information on diffusion lengths at the various band features. Qualitatively, it shows that these lengths are made shorter as the particle energy increases.

The implications of this work extend beyond the facilitation of a band structure probe in showing that band structure has a clear role in the photovoltaic effect.

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