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Field and temperature dependencies of the quantum efficiency of GaAs and GaP Schottky diodes

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Abstract. An experimental and theoretical study of GaAs and GaP Schottky photodiode quantum efficiency is reported. The quantum efficiency was investigated as a function of temperature in the 80–360 K interval and as a function of electric field in the space-charge region in the 15–50 kV cm^{-1} interval. The photocurrent is found to increase strongly with temperature, by a factor of three for GaP diodes and by a factor of six for GaAs diodes. We believe that this is evidence of a high concentration of imperfections in the space-charge region. These imperfections manifest themselves only in photoelectric properties. Such defects act as traps and capture both photoelectrons and photoholes. At low temperatures, most of the pairs recombine, but some fraction of them escape from the traps due to thermal excitation and give an electric current which rises with temperature. The time of the capture has to be of the order of the carrier drift time, 10^{-11} s. The electric field dependence of the quantum efficiency is also evidence of the high trap concentration. We believe that this is due to a field-induced shift of the carrier energy level in the trap. At high temperature, the photon energy and electric field dependencies of the photocurrent tend towards saturation.

1. Introduction

Most of the research on the short-wavelength quantum efficiency of Schottky diodes based on III–V semiconductors has been carried out at room temperature [1, 2]. The temperature-induced changes in the quantum efficiency have been discussed in view of photosensor thermal stability [3]. For example, at high photon energies the variation of GaP photodiode quantum efficiency does not exceed 0.1% per degree over the temperature range 260–330 K [4].

In this paper we report a study of the temperature and field dependencies of the quantum efficiency of Ni–GaAs and Au–GaP surface-barrier structures over a wide temperature and electric field ranges. Very strong dependencies were observed in the spectral interval of semiconductor intrinsic absorption, which cannot be explained within the framework of known models. We have investigated different semiconductor materials (GaP and GaAs) with different metal contacts (Au and Ni, respectively) which have been fabricated in different conditions. An increase in the quantum yield with the temperature and electric field has been observed for both cases. The difference was only in the rate of increase for the GaAs and GaP structures.

We propose a model which assumes the existence of a very high concentration of traps in the space-charge region (SCR). Each defect can trap one or more electron–hole pairs. The defect concentration and capture cross section should be so high that the mean free path for trapping, L_t, is less than the SCR thickness, W ($L_t < W$). If we take $L_t \sim W \approx 10^{-5}$ cm, the product of the trapping cross section, σ_t, and the trap concentration, N_t, will be of the order of $N_t\sigma_t \sim L_t^{-1} \approx 10^5$ cm^{-1}. Furthermore, if we take $\sigma_t \sim 10^{-14}$ cm^2 (a typical atomic defect value for 100 K; see for example, [5]) we get $N_t \sim 10^{19}$ cm^{-3}. Such a high defect concentration should manifest itself in other properties (e.g. the capacitance) and this is not observed. We have studied the electric and photoelectric properties of the structures (capacitance–voltage (C–U), current–voltage–temperature (I–U–T), and photocurrent–photon energy (I_{ph}–$h\nu$) characteristics). All of these characteristics coincide with the predictions of the well-known theories. Therefore the observed relatively strong temperature and electric field dependencies of the photocurrent are really intrinsic properties of the materials, and are not a result of extrinsic effects due to the processing of the devices.

2. Experimental procedure

The test samples were Au–n-GaP and Ni–n-GaAs surface-barrier structures. The structures consist of a semiconductor wafer with an Ohmic contact (In) on one side, and a semitransparent barrier contact (a layer of Au or Ni) on the other side. The GaAs wafer is an n-epitaxial layer ($n \approx 2 \times 10^{15}$ cm^{-3}) grown on an n-substrate. The GaP wafer has an electron density $n = (1$–$3) \times 10^{17}$ cm^{-3} (300 K). The GaAs epilayer has $n \approx 2 \times 10^{15}$ cm^{-3} (300 K). The wafers were oriented along the (100) crystallographic plane for GaAs and along the (111) crystallographic plane for GaP. The barrier contact was fabricated by means of chemical deposition of Au or Ni. The thickness of the wafers is 0.02 cm, and their surface area is $\approx$0.05 cm^2. The structures were not coated with any antireflection film.

The potential barrier heights determined by various techniques (C–U, I–U, and I_{ph}–$h\nu$ studies) are the same: $\phi_B = 0.89$ V (300 K) and $\phi_B = 0.96$ V (extrapolation to 0 K) for the GaAs structures, and $\phi_B = 1.19$ V (300 K) and $\phi_B = 1.25$ V (extrapolation to 0 K) for

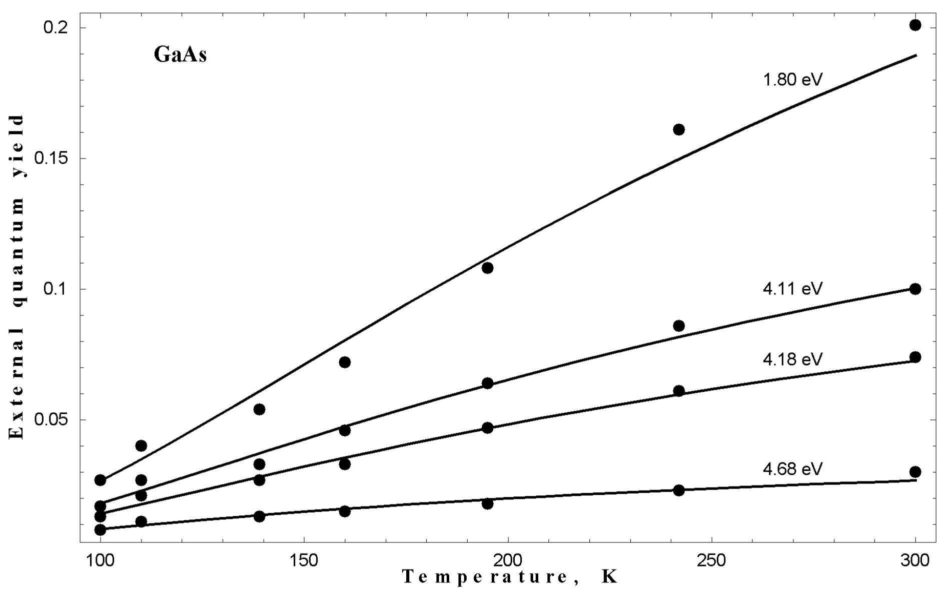


Figure 1. The external quantum yield, γ, of the Ni–GaAs Schottky diode as a function of the temperature for several photon energies. The points represent the experimental results; the curves are drawn according the model.

the GaP structures. As was shown in [6], the current–voltage characteristics of the diodes are consistent with those expected from thermionic emission theory, i.e. the current through the structures is determined by the thermionic emission and the tunnelling process is negligible.

We studied the temperature and electric field dependencies of the short-wavelength quantum efficiency of these structures over the photon energy interval 2–6 eV. The samples were illuminated by a mercury lamp through a monochromator or by the integral light of a deuterium lamp. The effective optical absorption length $L_\nu = \alpha^{-1}$ (α is the optical absorption coefficient) is much shorter than the length of the photoelectric active region in the ranges 3–5 eV (the GaP case) and 2–5 eV (the GaAs case).

The temperature dependencies we measured using a regular temperature chamber with a sapphire window. The temperature interval was 80–360 K. The electric field interval was 15–50 kV cm^{-1} which corresponds to reverse bias in the range 0–6 V. The reverse-bias circuit and the photocurrent registration circuit were separated from each other. The test structures were studied under short-circuit conditions for the photocurrent. The quantum efficiency (external quantum yield) was determined from the standard formula

$$\gamma = \frac{Ih\nu}{eP} \tag{1}$$

where I is the photocurrent, P is the incident light power, e is the electron charge, and $h\nu$ is the photon energy.

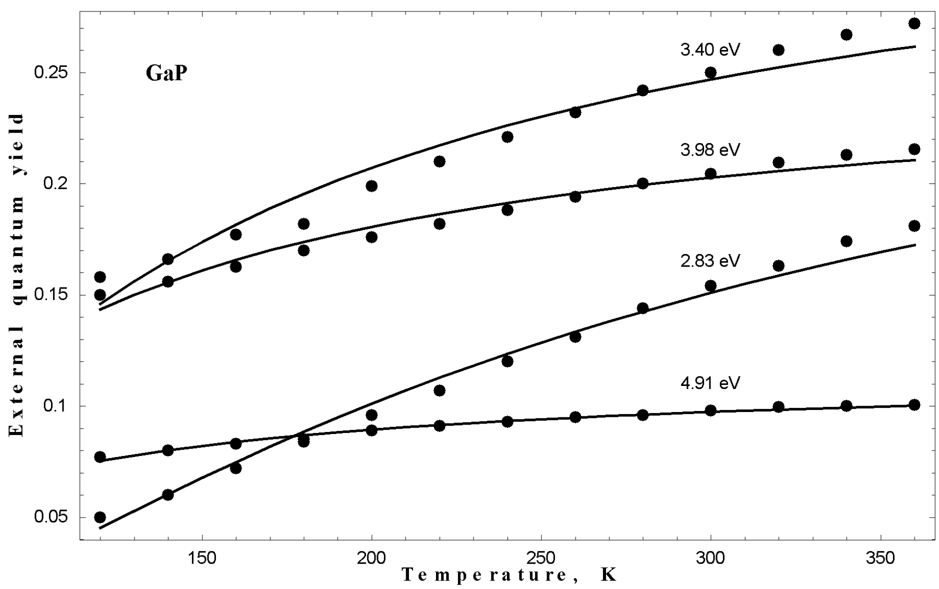


Figure 2. The external quantum yield, γ, of the Au–GaP Schottky diode as a function of the temperature for several photon energies. The points represent the experimental results; the curves are drawn according the model.

3. Results

In figures 1 and 2 we present the external quantum yield, γ, of Ni–GaAs and Au–GaP Schottky diodes as a function of the temperature for several photon energies.

For GaAs, when the temperature is raised from 100 to 300 K the quantum efficiency of the structures increases by approximately a factor of six for all photon energies.

For GaP, when the temperature is raised from 80 to 360 K the quantum efficiency of the structures increases differently for different photon energies.

The dependencies are stronger for Ni–GaAs structures. At high temperatures the temperature dependencies of the quantum efficiency tend towards saturation for all photon energies.

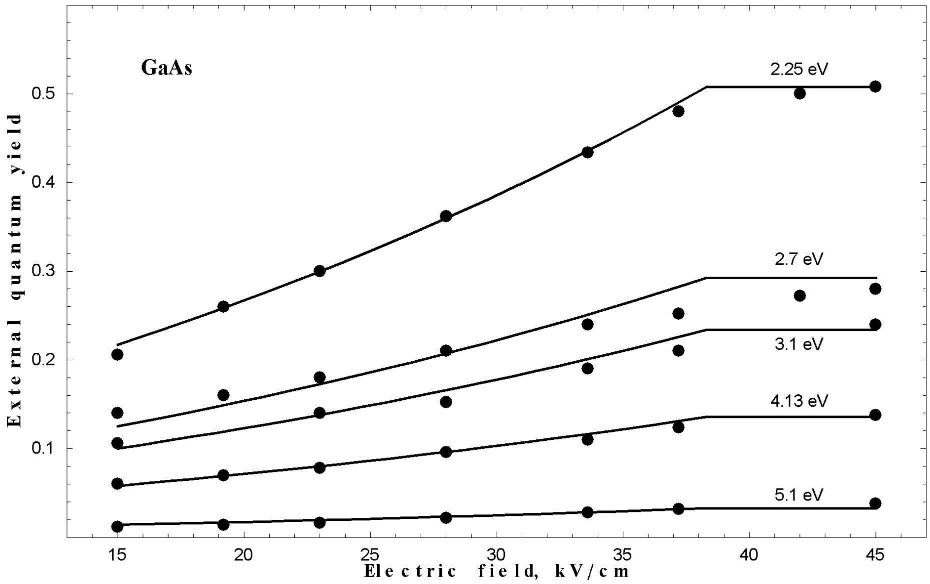


Figure 3. The external quantum yield, γ, of the Ni–GaAs Schottky diode as a function of the maximum electric field inside the SCR for several photon energies at $T = 300$ K. The points represent the experimental results; the curves are drawn according the model.

In figure 3 we present the external quantum yield, γ, of the Ni–GaAs Schottky diode as a function of the maximum electric field inside the SCR for several photon energies at $T = 300$ K. The quantum efficiency is found to depend strongly on the contact electric field in the SCR. As the electric field is raised from 15 to 45 kV cm^{-1} the quantum efficiency of the structures increases by a factor of 2.3 for all photon energies.

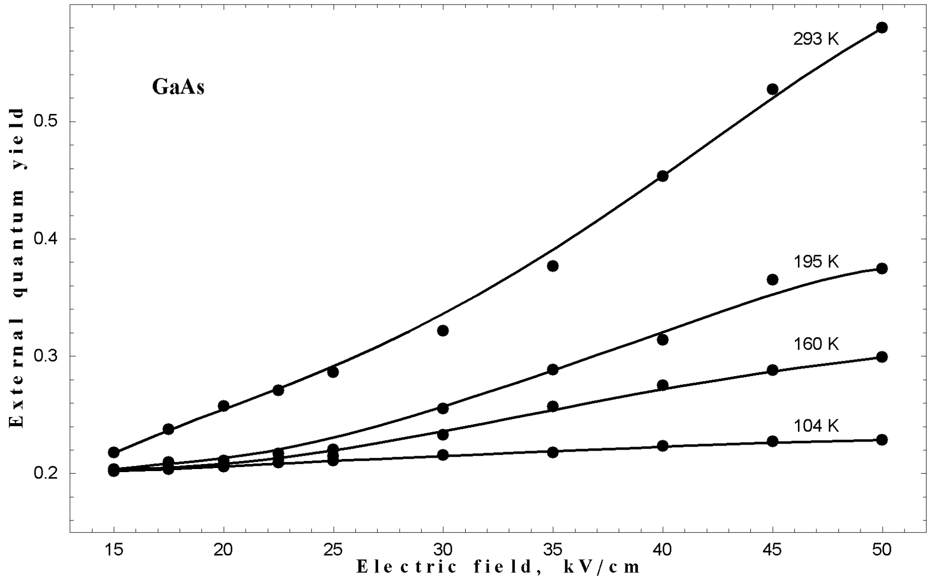
At high electric field, the dependence of the quantum efficiency tends towards saturation for all photon energies.

In figure 4 we present the external quantum yield, γ, of the Ni–GaAs Schottky diode versus the electric field (15–50 kV cm^{-1}) for several temperatures. The sample was illuminated by the integral light of a deuterium lamp.

These results show that the dependence of the quantum efficiency on the electric field in the SCR presents for low temperatures also, and the greater the temperature, the stronger the dependence of the quantum efficiency on the electric field.

4. The mechanisms of the temperature and field dependencies of the quantum efficiency

According to our experiments, the quantum efficiency of the photoelectric conversion depends strongly on the temperature and reverse bias. There are a number of models describing



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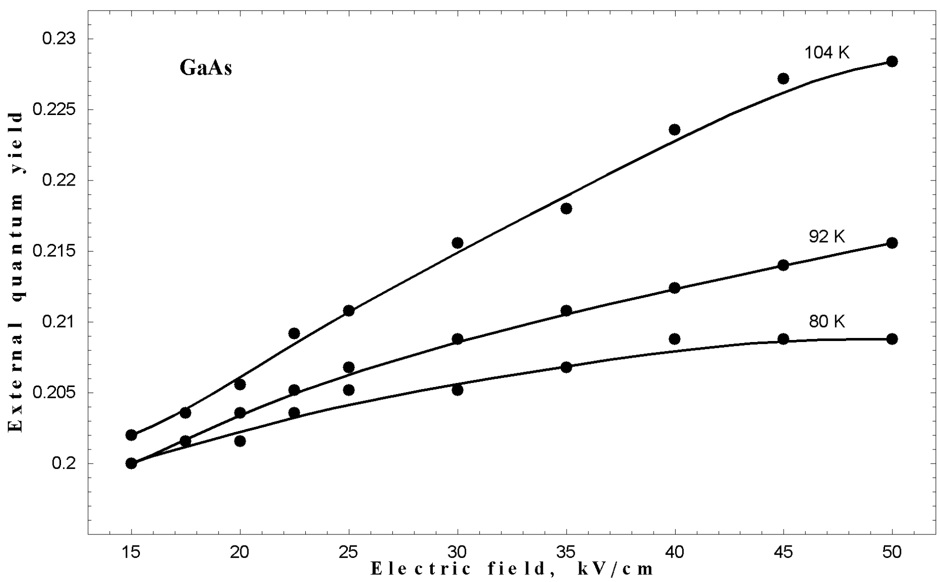

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Figure 4. The external quantum yield, γ, of the Ni–GaAs Schottky diode as a function of the maximum electric field inside the SCR for several temperatures. The sample was illuminated by a full deuterium lamp spectrum. The points represent the experimental results; the curves are Bezier splines.

the photoelectric process and predicting temperature and field dependencies of the quantum efficiency. Our estimations show that these models cannot explain the results obtained. For example, the dependence of the quantum efficiency on the electric field was explained earlier [7, 8] in terms of an expansion of the space-charge region with increasing applied reverse bias and the corresponding increase in the fraction of electron–hole pairs separated by the contact electric field. However, this picture is valid only for photon energies close to the band gap, when the light absorption length L_ν exceeds the SCR thickness W. In our case the opposite condition, namely $L_\nu \ll W$, was satisfied, so the increase in the SCR width should in no way influence the quantum efficiency. The increase in quantum efficiency with increasing electric field could be related to the increase in the height of the potential barrier experienced by photoelectrons entering the metal, i.e., a reduction in the loss of photoelectrons. However, simple estimates show that this phenomenon could not have such a strong influence on the quantum yield as was revealed experimentally. Another possible mechanism for the dependence of the quantum efficiency on the applied bias is a change in the thickness of the dead layer on the surface of the semiconductor from which all the electrons are extracted into the metal by image forces. However, the width of this layer amounts to a few tens of ångströms and does not depend strongly on the reverse bias. This means that the change in this width for photon absorption lengths of the order of a few hundred ångströms can in no way explain the substantial change in the observed photocurrent.

It is ordinarily assumed that if the surface recombination and the thermionic emission of photoelectrons into the metal are neglected, then the contact electric field separates all thermalized photoelectrons and photoholes. In our case these factors are negligible and the quantum efficiency should not depend on the temperature. As follows from the experiment, the quantum efficiency does depend on the temperature.

We consider that the large increase in the quantum efficiency with increasing electric field and temperature can be explained according the following model. The model assumes the presence of fluctuations in the profile of the bottom of the conduction band and the ceiling of the valence band. In the contact electric field, this kind of fluctuation becomes a trap for electrons and for holes. Carriers of different sign become localized in close spatial regions, which may give rise to their recombination.

The quantum efficiency is essentially the probability that a photon will be absorbed in the semiconductor with the creation of an electron–hole pair which is then separated by the contact electric field and which contributes to the photocurrent. The following formula gives this probability as a product of the probabilities of three successive events:

$$\gamma = (1 - R)(1 - \delta_{hot})(1 - \delta_{therm}) \tag{2}$$

where: $1 - R$ is the probability that the photon will not be reflected by the surface and will be absorbed by the semiconductor (R is the light reflection coefficient); $1 - \delta_{hot}$ is the probability that the electron–hole pair produced by a photon will cool down in the SCR, i.e., it will be influenced by the contact field (δ_{hot} is the coefficient representing the loss of hot carriers, which depends on the photon energy and the properties of the semiconductor); and $1 - \delta_{therm}$ is the probability that the cooling electron–hole pair will be separated by the contact field and will contribute to the photocurrent (δ_{therm} is the coefficient representing the loss of thermalized carriers; it is determined by the recombination of carriers captured by the traps, and depends on both the temperature and the electric field in the SCR).

In the case of Boltzmann statistics,

$$1 - \delta_{therm} = \exp\left(-\frac{\Delta E(\varepsilon)}{kT}\right) \tag{3}$$

where ΔE is the localization energy of the electron–hole pairs, ε is the electric field in the

SCR, k is Boltzmann's constant, and T is the temperature. The quantum efficiency given by equation (2) then takes the form

$$\gamma = (1 - R)(1 - \delta_{hot}) \exp\left(-\frac{\Delta E(\varepsilon)}{kT}\right). \quad (4)$$

We note that recombination losses on the surface were neglected because they are small in this particular series of samples.

The concentration of thermalized free carriers increases with increasing temperature because of the thermal dissociation of electron–hole pairs captured by the traps. Consequently, the quantum efficiency increases with increasing temperature. The temperature dependence of the quantum efficiency was used to determine the carrier localization energy, ΔE_0, in the absence of bias across the structure by fitting the experimental points with expression (4).

For the GaAs structures, ΔE_0 does not depend strongly on the photon energy. Fitting gives $\Delta E_0 = 25, 22, 21$, and 15 meV for 1.8, 4.11, 4.18, and 4.68 eV. For the GaP structures, ΔE_0 does depend on the photon energy: $\Delta E_0 = 20.8, 9.1, 6.0$, and 4.4 meV for 2.83, 3.40, 3.98, and 4.91 eV.

The fitting of the temperature dependencies was the starting point for the calculation of the field dependencies of the quantum efficiency. The proposed mechanism for the dependence of the quantum efficiency on the applied reverse bias may be described as follows. As the reverse bias increases, i.e., the contact electric field increases, the band slope in the SCR is found to increase, which in turn leads to a reduction in the localization energy of the electron–hole pair in the trap. For a given temperature, this reduction in the localization energy leads to an increase in the concentration of thermalized free carriers and, consequently, an increase in the quantum efficiency.

The dependence of the localization energy on the contact electric field can be represented as

$$\Delta E(\varepsilon) = \Delta E_0 - [\mathcal{E}(\varepsilon) - \mathcal{E}(\varepsilon_0)] \quad (5)$$

where ΔE_0 is the localization energy in the absence of the reverse bias when the electric field ε in the SCR is $\varepsilon_0 = 15$ kV cm^{-1}, and $\mathcal{E}(\varepsilon)$ is the level energy measured from the bottom of the well. We assigned $\Delta E_0 = 22$ meV for all of the GaAs structures. Thus, in this case we use a single fitting parameter to adjust both the temperature and field dependencies. In the case of GaP structures, one needs to take a different value of ΔE_0 for each photon energy.

Using the triangular potential well with infinite walls as the initial coarse approximation, we obtain

$$\mathcal{E}(\varepsilon) = \xi_1 \left(\frac{\hbar^2 \varepsilon^2}{2m}\right)^{1/3} \quad (6)$$

where $\xi_1 \approx 2.34$ is the first root of the Airy function, $\hbar$ is the reduced Planck's constant, and m is effective mass of an electron.

Using formulae (4)–(6) and the light reflection coefficient, one can determine the hot-carrier-loss coefficient δ_{hot}, which is shown in figure 5. We present the reflection coefficient [9] and the external quantum yield [1] for GaAs in figure 5, also.

It follows from (5) and (6) that the localization energy decreases rapidly with increasing contact electric field in the SCR, which in turn leads to an increase in the quantum efficiency. When the contact field is so strong that the localization energy is zero, the quantum efficiency ceases to depend on the electric field. The triangular-well model with infinite walls is, of course, too approximate and disregards several factors, e.g., tunnelling through the potential barrier. This is why each theoretical curve shows a 'knee' as it enters the saturation regime.

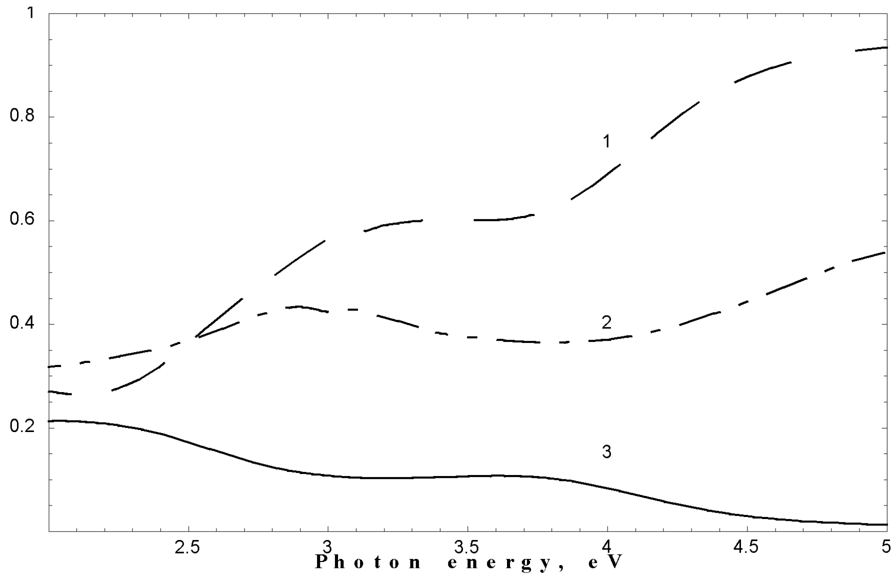

Figure 5. The hot-carrier-loss coefficient, δ_{hot} (curve 1), the light reflection coefficient, R (curve 2), and the external quantum yield, γ (curve 3), versus the photon energy for the Ni–GaAs Schottky diode.

5. Conclusions

We have carried out an experimental investigation of the quantum efficiency of the photoelectric effect in the short-wavelength region of the spectrum as a function of temperature and the applied reverse bias in GaAs and GaP Schottky diodes. We found strong temperature and electric field dependencies of the quantum efficiency. In the spectral region where the light absorption length is much smaller than the width of the space-charge region, these results are of great interest. They show the existence of imperfections in the space-charge region which could not be revealed by the usual methods (via capacitance–voltage characteristics etc). We proposed a model involving fluctuation traps in the SCR. As the temperature increases, the density of free thermalized photocarriers increases as a result of thermal dissociation of electron–hole pairs trapped by the capture centres, and therefore the higher the temperature, the higher the quantum efficiency of the photoelectric conversion; this continues until the traps are completely emptied.

As the reverse bias increases, i.e. the contact field increases, the band slope in the SCR is found to increase, which leads to a reduction in the localization energy of the electron–hole pairs in the trap and to an increase in the quantum efficiency. The model proposed allows us to reproduce the temperature and field dependencies using a single phenomenological parameter.

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