

Relation between photoreflectance excitation and absorption spectra for GaAs and GaN films

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Photoreflectance excitation (PRE) spectroscopy is shown to be a suitable method to investigate semiconductor materials in the near-infrared to near-ultraviolet spectral range. The investigation of a GaAs and a GaN bulk film demonstrates the applicability of this method even up to room temperature. For both materials, the line shape analysis suggest a nonlinear relation between the PRE and the absorption line shapes, leading to a reduction of the excitonic peak height in the PRE spectra compared to the absorption spectra. To keep this reduction as small as possible, the pump power should be on the order of the probe power or smaller. © 2003 American Institute of Physics. [DOI: 10.1063/1.1529290]

I. INTRODUCTION

In 1987, Shen and co-workers introduced a spectroscopic method called photoreflectance excitation (PRE) spectroscopy.¹ In contrast to conventional photoreflectance (PR) spectroscopy, where the pump wavelength is fixed and the probe wavelength is varied, PRE spectra are measured with a fixed probe wavelength and a variable pump wavelength. Since the PR modulation mechanism is often based on the screening of the built-in electric field by electron-hole pairs generated by the pump light,² the modulation voltage and therefore the amplitude of the PRE signal depends on the number of pump photons absorbed within a space-charge layer near the surface. Consequently, the PRE spectrum should be related to the absorption spectrum of the respective sample. Shen *et al.*¹ applied this method to investigate a GaAs/(Al,Ga)As single quantum well at low temperatures. The obtained PRE line shape was very similar to the one measured by photoluminescence excitation (PLE) spectroscopy. Only one additional letter was published after 1987 using PRE spectroscopy for the characterization of ZnSe/GaAs(001) interface properties.³ However, the relation between the PRE and absorption line shape was not discussed.

There are several advantages of PRE compared to PLE. First, in order to excite the PRE signal, less optical power is required than for PLE. Therefore, the applicability of monochromatized white light as a tunable pump in PRE is less restrictive. This allows us to apply PRE to a variety of semiconductor materials and, at the same time, in spectral ranges, where no tunable lasers are readily available. Second, PRE signals can be measured over a wide temperature range up to room temperature, whereas PLE usually requires a lower temperature in order to have sufficiently large PL signals. Third, the probe wavelength can be set to any value of the corresponding PR spectrum with a sufficiently large PR amplitude. No detection window near the probe wavelength has

to be excluded as is usually done for PLE spectroscopy. The main advantage of PRE compared to PR spectroscopy is the simpler line shape. However, so far, the relation between the PRE and absorption line shape has not been clarified.

In the present article, we apply the method of PRE spectroscopy to two different material systems. We present temperature-dependent experimental results for a GaAs film on GaAs and a GaN film on SiC. The relation between the PRE and absorption line shape is discussed for both materials based on a recent model for the description of the PR signal strength.⁴

II. EXPERIMENT

The first of the two investigated samples consists of a 5- μm -thick, Si-doped GaAs film grown by solid-source molecular-beam epitaxy (MBE) on a semi-insulating GaAs substrate. The electron density was determined to be about $2 \times 10^{15} \text{ cm}^{-3}$. The second sample consists of a 1.7- μm -thick GaN layer deposited directly onto 6H-SiC(0001) by reactive MBE. The background electron concentration amounts to $2 \times 10^{17} \text{ cm}^{-3}$. In both cases, the carrier density was measured by capacitance-voltage profiling.

The experimental setup shown in Fig. 1 employs two monochromators for the PR and PRE experiments and is very similar to the ones described in Refs. 1 and 4. The PRE spectra are recorded by measuring the PR signal $\Delta R/R$ as a function of energy of the pump light. At the same time, the probe light energy is kept constant at a spectral position corresponding to a large PR signal, which is usually the position of the dominant minimum of the PR spectrum. To remove spurious light, we record two spectra under the same modulation conditions, one with and one without the probe light, and subtract both spectra from each other. For the investigation of the GaAs (GaN) sample, we use two 100 W halogen lamps (a 150 and a 75 W Xe arc-lamp) as white light sources to generate the pump and the probe light. We do not control the pump intensity by neutral density filters as it was realized

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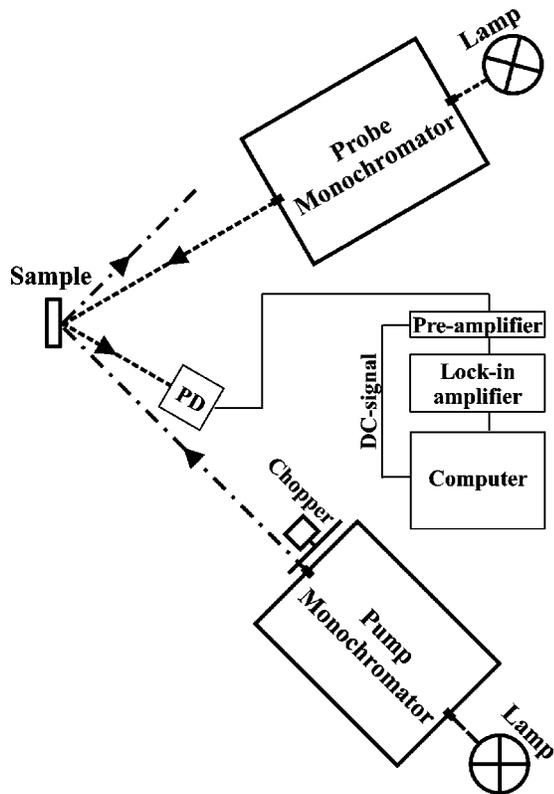


FIG. 1. Schematic diagram of the PRE setup.

in Ref. 1, because the monochromatic pump power shows only small variations over the spectral ranges of interest. The samples are placed within a He-bath cryostat allowing temperature control between 5 and 400 K. The probe light reflected from the sample is detected with an UV-enhanced Si photodiode. The signal is preamplified and recorded by a conventional lock-in technique.

III. PHOTOREFLECTANCE AND PHOTOREFLECTANCE EXCITATION SPECTRA

The measured PR and PRE spectra of the GaAs sample are shown in Fig. 2 for different temperatures as indicated. For all temperatures, the PR spectra in Fig. 2(a) exhibit Franz-Keldysh oscillations for energies above the gap. In addition, the PR spectrum at $T=80$ K shows a strong excitonic resonance at about 1.507 eV. This resonance is strongly reduced at higher temperatures. The small structures seen in the PR spectrum at 200 and 295 K at around 1.46 and 1.42 eV, respectively, can be attributed to a residual influence of excitonic effects, but may also be due to the influence of an electric-field inhomogeneity as suggested in Ref. 5. As shown in Fig. 2(b), it is possible to measure PRE spectra not only at low temperatures, but also at higher temperatures up to room temperature. At 80 K, the PRE spectrum exhibits a clear excitonic peak as observed in the corresponding PR spectrum. At higher temperatures, the peak intensity is reduced, and it disappears at room temperature.

We also measured the PR and PRE spectra of a GaN film, which are shown in Figs. 3(a) and 3(b), respectively, for different sample temperatures as indicated. As for GaAs, the

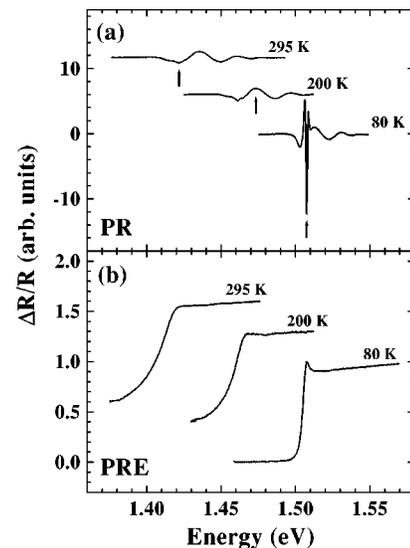


FIG. 2. (a) PR and (b) PRE spectra for different temperatures as indicated measured near the fundamental gap of the GaAs film. The positions of the fixed probe energy for the PRE spectra in (b) are marked in (a) by arrows. For a better comparison, the PR spectra in (a) are normalized with respect to the first Franz-Keldysh oscillation and vertically shifted to each other. The PRE spectra in (b) are also normalized and vertically shifted to each other.

PRE spectra for GaN can be measured over the whole temperature range. At 5 K, the spectrum exhibits two excitonic peaks. The first one corresponds to a superposition of the *A* and *B* exciton, which are not resolved. Due to the thermally induced, tensile strain of about 0.2% in the film, the energy separation of the *A* and *B* exciton should be about 2–3 meV,⁶ which is much less than the broadening of the peaks. The second peak with an energy separation of about 18 meV to the first one is attributed to the *C* exciton. With increasing temperature, the excitonic peaks become less pronounced and are barely visible at room temperature.

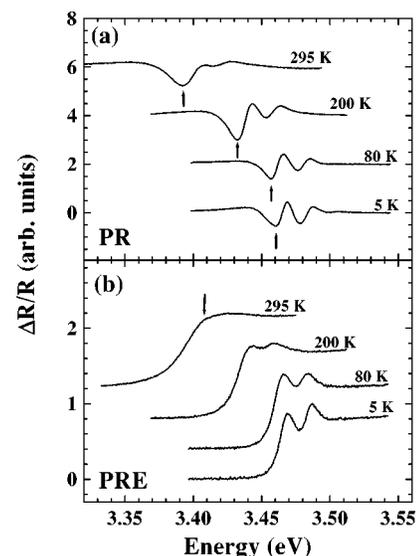


FIG. 3. (a) PR and (b) PRE spectra for different temperatures as indicated measured near the fundamental gap of the GaN film. The positions of the fixed probe energy for the PRE spectra in (b) are marked in (a) by arrows. For a better comparison, the spectra are normalized and vertically shifted to each other.

At low temperatures, the PR line shape of the GaN sample is dominated by excitonic effects. When the PR spectra measured at 5 and 80 K are fitted using the often applied derivative functional form of Aspnes⁷ (E energy, E_0 transition energy, A amplitude factor, ϕ phase, and Γ broadening parameter)

$$\frac{\Delta R}{R}(E) = \Re \left[\frac{A e^{i\phi}}{(E - E_0 + i\Gamma)^n} \right] \quad (1)$$

with an exponent $n=3$, the derived exciton-transition energies differ by (6–8) meV from the values obtained from the PRE spectra. This is an indication that a more complex line shape model has to be applied to fit the experimental PR data. At room temperature, the PR line shape deviates significantly from the low-temperature one, showing only one dominant minimum at about 3.392 eV. The structure seen at about 3.41 eV is attributed to the C exciton, followed by typical, but rather weak Franz–Keldysh oscillations extending up to 3.58 eV [only partly shown in Fig. 3(a)]. Therefore, we attribute this line shape to an intermediate-field Franz–Keldysh type,⁸ but with a residual excitonic influence. In this case, fitting the line shape with a derivative functional form as given by Eq. (1) is not reasonable, because the line shape is neither purely excitonic nor purely low-field Franz–Keldysh type. However, taking the energy of the dominant minimum of the PR spectrum as the exciton-transition energy would result in a rather significant error as seen from the corresponding PRE spectrum. The position of the first residual excitonic PRE peak at 3.408 eV marked in Fig. 3(b) by an arrow differs considerably from the position of the PR minimum.

IV. LINE SHAPE OF PHOTOREFLECTANCE EXCITATION SPECTRA

For both materials, a direct measurement of the absorption coefficient requires the removal of the substrate. We therefore compare the measured PRE spectra to data in the literature for high-quality materials. For the GaAs film, the observed excitonic peak height as well as the slope of the non-excitonic high-energy part of the PRE spectrum are smaller than in reported experimental absorption spectra.^{9,10} In the GaN film, the excitonic peaks are also more distinct in reported experimental absorption spectra^{11,12} than in our PRE spectra. In order to calculate the PRE line shape, it is necessary to determine the relation between the PRE signal and the absorption coefficient of the sample as well as the modulation parameters such as pump and probe light intensity. We are using a line shape model based on a simple transport theory for the surface photovoltage^{4,13} induced by the pump and the probe light making the following conjectures. First, the modulation mechanism of the PR signal is assumed to be based on the photoinduced generation of electron-hole pairs and the screening of the surface electric field, i.e., electric-field modulation. Second, the electric field and the band bending in the depletion layer near the surface can be described by the Schottky model. Third, the modulation is assumed to be steady state, i.e., the typical relaxation and drift times are short compared to the modulation period. Fourth,

in the low-modulation limit, the PR amplitude can be set to be proportional to the surface modulation voltage V_m .^{14,15}

The photovoltage V_S can be derived from transport theory^{4,13} as

$$V_S = \frac{\eta k_B T}{e} \ln \left[\frac{J_{PC}}{J_{ST}(T)} + 1 \right], \quad (2)$$

where η is an ideality factor, k_B is Boltzmann’s constant, and $J_{ST}(T)$ is the saturation (dark) current density. J_{PC} denotes the photoinduced current density, which can be expressed as¹³

$$J_{PC} = \frac{eP\gamma(1-R)}{\hbar\omega} \left[1 - \frac{\exp(-\alpha W)}{1 + \alpha L_D} \right], \quad (3)$$

where P denotes the pump or probe intensity, γ is the quantum efficiency, R is the reflectivity at the surface, $\hbar\omega$ is the photon energy, α is the absorption coefficient, W is the width of the depletion layer, and L_D is the diffusion length of the minority carriers. The saturation current density is given by^{4,13}

$$J_{ST}(T) = \frac{A^{**}T^2}{1 + BT^{3/2}} \exp \left(- \frac{eV_F}{k_B T} \right), \quad (4)$$

where A^{**} denotes the modified Richardson constant, B is a constant related to the saturation velocity, and V_F is the surface Fermi voltage.

In PR and PRE measurements, both the probe and the pump light contribute to J_{PC} . The light intensity at the sample surface is modulated by a chopper with two states, pump on or pump off. The corresponding light levels P_{probe} (pump off) and $P_{\text{probe}} + P_{\text{pump}}$ (pump on) result in two photovoltages V_s^{off} and V_s^{on} . The modulation voltage V_m is then given by

$$V_m = V_s^{\text{on}} - V_s^{\text{off}} = \frac{\eta k_B T}{e} \left[\ln \left(\frac{J_{\text{probe}} + J_{\text{pump}}}{J_{ST}} + 1 \right) - \ln \left(\frac{J_{\text{probe}}}{J_{ST}} + 1 \right) \right]. \quad (5)$$

This expression can be transformed into

$$V_m = \frac{\eta k_B T}{e} \ln \left(1 + \frac{J_{\text{pump}}}{J_{\text{probe}} + J_{ST}} \right). \quad (6)$$

In the low-signal limit, the PRE signal, which corresponds to the amplitude of the PR signal $(\Delta R/R)_{\text{amp}}$, is proportional to V_m so that I_{PRE} can be described by

$$I_{\text{PRE}}[\alpha(E), P_{\text{pump}}, P_{\text{probe}}, T, V_F] = \left(\frac{\Delta R}{R} \right)_{\text{amp}} = C_1 V_m, \quad (7)$$

where C_1 is a constant depending on the actual line shape of the PR spectrum (e.g., Franz–Keldysh effect, first derivative excitonic line shape or third derivative line shape) and the broadening influenced by temperature and crystal quality. As seen from Eqs. (2)–(7), I_{PRE} is a function of the sample temperature, the probe and pump power, the surface Fermi voltage and, most importantly, the energy-dependent absorption coefficient $\alpha(E)$. For fixed values of P_{pump} , P_{probe} , V_F ,

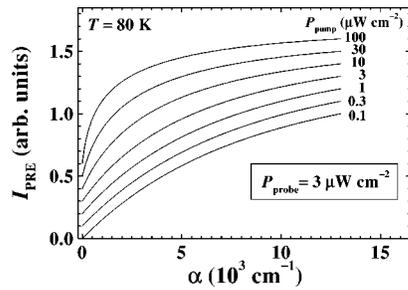


FIG. 4. Calculated PRE signal as a function of the absorption coefficient for GaAs. The curves are calculated for a fixed probe power of $3 \mu\text{W cm}^{-2}$ and different pump powers as indicated. The parameters for the calculation are $\eta=1$, $A^{**}=8 \times 10^4 \text{ A(mK)}^{-2}$, $B=3.3 \times 10^{-4} \text{ K}^{-3/2}$, $V_F=0.75 \text{ V}$, and $L_D=0.5 \mu\text{m}$. For a better comparison, the curves are normalized and vertically shifted to each other.

and T , the photoreflectance excitation line shape $I_{\text{PRE}}(E)$ is identical to the absorption line shape $\alpha(E)$, only if I_{PRE} is a linear function of α .

V. RELATION BETWEEN ABSORPTION AND PHOTOREFLECTANCE EXCITATION SPECTRA

In Fig. 4, the calculated dependence of I_{PRE} on the absorption coefficient based on Eqs. (2)–(7) is shown for the GaAs sample for a fixed probe power of $3 \mu\text{W cm}^{-2}$ and different pump powers as indicated. As seen from Fig. 4, the actual relationship between I_{PRE} and the absorption coefficient α is nonlinear, although for pump intensities $P_{\text{pump}} \ll P_{\text{probe}}$ the function $I_{\text{PRE}}(\alpha)$ shows only small deviations from a linear behavior. In this regime, the PRE line shape will be close to the absorption line shape. For larger pump intensities, $I_{\text{PRE}}(\alpha)$ increases with a large slope for small values of α and a much smaller slope for larger values of α . This nonlinearity results in a considerable reduction of the excitonic peak height in the PRE spectra in comparison to the absorption spectra. To keep this reduction as small as possible, it is important to minimize the nonlinearity of $I_{\text{PRE}}(\alpha)$, i.e., to keep the pump power as low as possible. Qualitatively similar results are obtained for GaN.

We calculated the absorption spectrum of the GaAs film from the experimental PRE spectrum for $T=80 \text{ K}$ in Fig. 2 using the calculated dependence of $I_{\text{PRE}}(\alpha)$ shown in Fig. 4. The resulting absorption spectrum is shown in Fig. 5. In

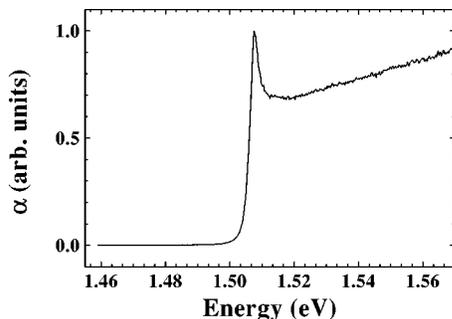


FIG. 5. Absorption spectrum of the GaAs film calculated from the experimental PRE spectrum measured at $T=80 \text{ K}$ in Fig. 2 using the calculated dependence of $I_{\text{PRE}}(\alpha)$ shown in Fig. 4. The experimental probe and pump power were estimated to be 3 and $10 \mu\text{W cm}^{-2}$, respectively.

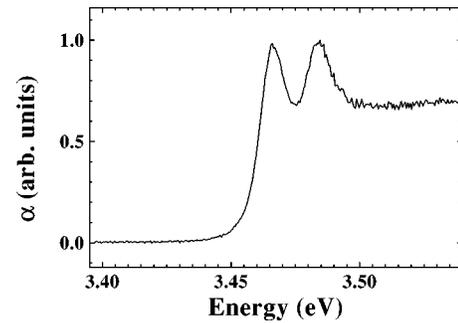


FIG. 6. Absorption spectrum of the GaN film calculated from the experimental PRE spectrum measured at $T=80 \text{ K}$ in Fig. 3. The experimental probe and pump power were estimated to be $50 \mu\text{W cm}^{-2}$. The parameters for the calculation are $\eta=1$, $A^{**}=2.4 \times 10^5 \text{ A(mK)}^{-2}$, $B=4.62 \times 10^{-5} \text{ K}^{-3/2}$, $V_F=0.7 \text{ V}$, and $L_D=0.0 \mu\text{m}$.

comparison to the experimental PRE spectrum, the excitonic peak in this calculated absorption spectrum is more pronounced in agreement with the reported experimental absorption data in Ref. 9. The result of a similar calculation for the GaN film is shown in Fig. 6. For GaN, the enhancement of the excitonic peaks in the calculated absorption spectrum in comparison to the PRE spectrum is less pronounced than for GaAs. This reduced enhancement is due to the higher doping level in the GaN film, which results in a smaller width of the space-charge layer. Further information on the calculation for GaN can be found in Ref. 16.

Although a qualitative agreement between the calculated absorption spectra determined from the PRE spectra and the experimental absorption spectra reported in the literature can be clearly observed, it appears to be rather difficult to obtain reliable quantitative absorption data from a PRE measurement alone. In the calculation, some parameters such as the surface Fermi voltage may differ from sample to sample. Therefore, these should be experimentally determined by an independent method. A better insight in the quantitative validity of the applied model can be only obtained by a direct comparison of the absorption spectra calculated from the PRE spectra and experimental absorption spectra measured on the same sample. However, this usually requires the removal of the substrate.

VI. CONCLUSIONS

We have demonstrated that PRE spectroscopy is not only applicable to previously investigated semiconductor single- or multiquantum-well structures, but also to bulk-like films of different material systems such as GaAs and GaN over a wide temperature range. The results of the line shape calculations indicate a nonlinear relationship between the PRE and the absorption line shapes leading to a reduction of the excitonic peak height for PRE in comparison with absorption spectra. This is confirmed by experimental results. To minimize this effect, the pump power should be kept as small as possible.

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