



Recent developments in spectroscopy of quantum structures

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Abstract

Two spectroscopic techniques, modulated reflectance spectroscopy and surface photovoltage spectroscopy, are being used increasingly to probe the electronic structure of low-dimensional semiconductors. We have found improved versions of these techniques: soft contact electroreflectance and soft contact surface photovoltage which offer operational advantages as well as extend the range of these spectroscopies. We also provide analytic formulation for extracting the transition parameters from the measured surface photovoltage spectrum of a quantum structure. © 2002 Published by Elsevier Science Ltd.

Keywords: Electroreflectance; Surface photovoltage; Quantum structures; Spectroscopy

1. Introduction

Semiconductor quantum structures are in common usage for optoelectronics as well as high-speed electronics. Electronic energy levels of quantum structures are important structural parameters because of their dependence on size, composition, strain, etc. [1–4]. A number of spectroscopic techniques: photoluminescence (PL) [5,6], photoluminescence excitation (PLE) [7,8], and absorption [9,10] have been in use to probe the electronic transitions. However, even though these techniques are widely used, they have some limitations. For example, while PL is the most widely used measurement on quantum structures, it shows mainly the transition between the lowest conduction subband and the highest valence subband and gives practically no information about the transitions between the higher lying subbands. PLE spectra do provide information about transitions between the higher lying subbands; however, one generally requires either a tunable laser or a lamp-monochromator combination source in addition to the PL setup for this type of experiment. Absorption

spectroscopy is simpler, yet the absorption of a single QW is too small for reliable spectroscopy and for most experiments the sample has to be a multi-quantum well (MQW) structure which is not always desirable (e.g. in the case of strained QWs). These limitations are by and large overcome in the techniques which have come to be used widely recently, namely (a) modulated reflectance spectroscopy [11–15] and (b) surface photovoltage (SPV) spectroscopy [16,17]. As such these techniques were developed initially for probing the electronic structure of bulk semiconductors. However, their full potential has come to be realized with the advent of quantum structures and their applications, and the need for very precise determination of transition energies and related characteristics of single quantum well. There are several reviews, which are available in the literature and deal with these spectroscopies [11–17]. In this paper, we review some of the salient features of these spectroscopies and present some of our contributions with special emphasis on SPV. Spectroscopy principles are illustrated with applications to bulk semiconductors (n GaAs and p GaAs), and quantum structures: single QW (GaAs/InGaAs/GaAs) and quantum dots (InGaP on GaP). The quantum structures used in this work were synthesized in our laboratory using metalorganic vapor phase epitaxy.

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2. Basic aspects

2.1. Modulated reflectance spectroscopy

Reflectance spectrum of a semiconductor is a broad slowly varying function of photon energy. Features due to critical points in the band structure, such as the onset of band-to-band transitions, are superposed on the structureless background and cannot be separated accurately. Modulation spectroscopy measures a derivative of the dielectric response. As a result, the broad background disappears and sharp features corresponding to the critical points dominate the spectrum $\Delta R/R$, where ΔR is the modulation induced reflectance change. In case of a quantum well, sharp features in the modulated reflectance spectrum correspond to transitions between the subband levels in the conduction band and valence band of the well. Although different forms of perturbations have been investigated for modulation spectroscopies, periodically varying electric field is generally used to perturb the complex dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$. Perturbation changes the dielectric ε by $\Delta\varepsilon = \Delta\varepsilon_1 + i\Delta\varepsilon_2$ such that $\Delta R/R = a\Delta\varepsilon_1 + b\Delta\varepsilon_2$ and the resulting spectrum is called electroreflectance (ER).

2.2. Surface photovoltage spectroscopy

In surface photovoltage measurement, periodically chopped light beam illuminates the sample surface (See Fig. 1a). For photon energy greater than band to band transitions, surface photovoltage results because of photogeneration of electrons and holes and their separation under the built in surface electric field. Thus, the SPV spectrum nearly resembles the absorption spectrum. At first instance, it appears that magnitude of the surface photovoltage should be equal to the static change in the band bending. However, we shall show below that it is more realistic to consider the generated

photovoltage to be equivalent to an open circuit voltage, much like in a metal–semiconductor diode, which provides dynamic balance between the current components such that the net current is zero. A simple relation then expresses

$$\text{SPV} \cong V_{oc} = \frac{kT}{q} \ln \left(1 + \frac{I_{ph}}{I_0} \right), \quad (2.1)$$

where I_{ph} is the photocurrent generated by absorption of photons, I_0 is the dark current in the structure, k is the Boltzmann constant and T is the temperature. While this formulation seems adequate for the bulk semiconductor [18], since the electrons and holes are essentially free to move after photogeneration in the bulk material, but how do the photocarriers separate when we excite them selectively within the quantum well where they are localized spatially by potential barriers. Our experiments [19] show that in the case of QW, separation of charge carriers from the QW into the barrier regions occurs mainly by thermal emission at room temperature. At low temperatures, there can be significant field assisted tunneling of the carriers out of the QW followed by separation depending on the magnitude of electric field in the region of the QW.

3. Experimental aspects of ER and SPV spectroscopies

Electroreflectance is obtained by measuring reflected light signals I_0R and $I_0\Delta R(\omega)$ under the application of periodic electric field varying with angular frequency ω . A popular scheme of varying the electric field uses a chopped pump light beam, of photon energy larger than the band gap, to create electron–hole pairs which move under the influence of surface electric field and modify the surface field with the periodicity of light chopping. $\Delta R/R$ spectrum is measured using a steady probe light beam in the required wavelength range. This scheme

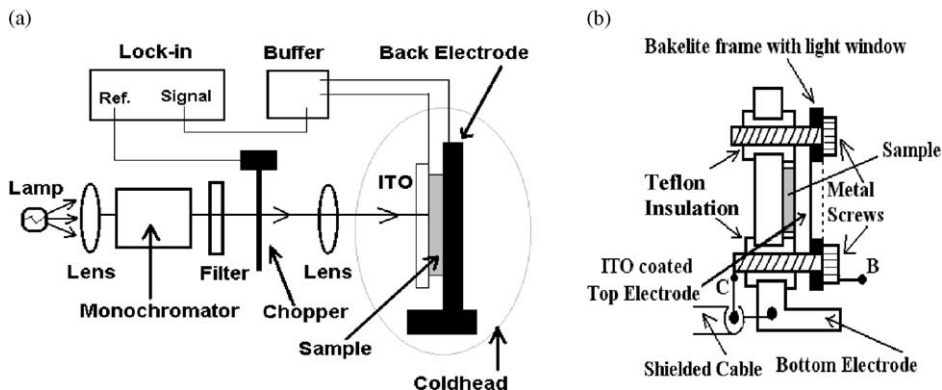


Fig. 1. Schematic diagram of (a) experimental set up for surface photovoltage spectroscopy and (b) detail of sample holder for soft contact mode.

known as photoreflectance (PR) has limitations, particularly due to PL at low temperatures, which can be overcome by the dual chopping schemes (DCPR) [20–22]. Although there are many schemes of measuring electroreflectance under the direct application of periodically varying electric field [11–14], the scheme which has come to be preferred by researchers is contactless electroreflectance (CER) [23]. The sample is placed in a capacitor like arrangement to apply the electric field. Sample is mounted on L shaped copper plate which is the back electrode. Top electrode is a transparent conducting thin film of indium–tin-oxide (ITO) coated on glass plate, which faces the sample. The light source consists of 150 W quartz halogen lamp and monochromator. The probe light beam passes through the glass plate and the ITO film both during the incidence and after the reflection. The reflected light is detected with Ge diode and lock in amplifier for $I_0\Delta R$ and directly with a dc-meter for I_0R . Generally, $I_0\Delta R$ is three to four orders of magnitude smaller than I_0R . In conventional CER [23], the separation between the sample surface and the ITO surface is a fraction of a mm. The modulating voltage necessary for the measurement depends on the gap width and is generally in excess of a kilovolt for useful CER signal. In our experiments, the ITO electrode is made to touch the sample (Fig. 1b). This improvisation reduces the magnitude of the ac voltage to less than one volt or even smaller in some cases and is a great advantage. We call this arrangement soft contact mode electroreflectance (SCER) [24]. For the SPV measurement, the basic arrangement is shown in Fig. 1a. A light chopper is introduced in the path of the light beam from the monochromator incident on the sample. The SPV is picked up from the ITO and the copper electrodes using shielded wires, passed through a high impedance unity gain buffer amplifier and measured with lock-in amplifier. Compared to non-contact SPV schemes, soft contact mode of SPV (SCSPV) measurement also has distinct advantages such as

enhancement of sensitivity by nearly a factor of 10^3 which makes it possible to measure even very weak SPV signals. For variable temperature measurements, the copper sample holder is clamped on to the cold finger of a closed cycle refrigerator.

4. Spectral shape analysis of ER and SPV

Fig. 2 shows typical SPV and ER spectra of a strained GaAs/InGaAs/GaAs QW. Apart from the feature at the band edge of GaAs at ~ 877 nm in each spectrum, we see sharp features corresponding to various QW transitions. We see strong correspondence between the two spectra. To extract transition energies from various features, the following procedures have been adopted.

With electric field modulation, the change $\Delta\varepsilon$ for free e–h pairs is proportional to third derivative of ε with respect to photon energy, while for localized excitations such as impurities, excitons and quantum wells, the change $\Delta\varepsilon$ is proportional to first derivative of ε with respect to photon energy. Aspnes [13] showed that in all these cases, a mathematical function can be used to represent the ER spectral line shape

$$\frac{\Delta R}{R}(E) = \text{Real} \left[\frac{a_j e^{i\theta_j}}{(E - E_{0j} + i\Gamma_j)^m} \right], \quad (4.1)$$

where E_{0j} is the j th critical point energy, Γ_j is the corresponding broadening factor, a_j is the amplitude and θ_j the phase factor. The value of parameter m is 2.5 for free e–h excitations and is 2 for localized excitations. In the cases, where the line shape function is inhomogeneously broadened, $m=3$ may provide a better choice. Ghosh et al. [25] have recently offered alternative mathematical line shape function which could be advantageous.

There is no universally accepted method for obtaining the transition energy values from the features in the SPV spectra. We have developed a method [24] to obtain the

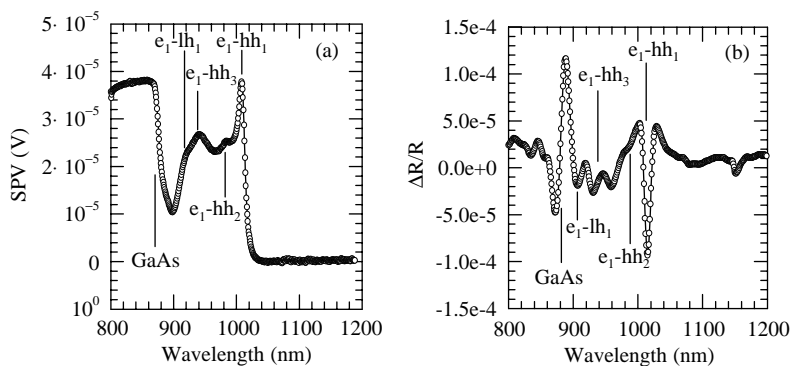


Fig. 2. (a) SPV spectrum of a GaAs/In_xGa_{1-x}As/GaAs ($x \sim 0.2$) single quantum well (~ 100 Å) sample at room temperature and (b) corresponding ER spectrum of the same sample at room temperature.

transition parameters, which applies exactly to the QW spectra and only operationally to the bulk semiconductor spectra. In order to obtain the necessary relation we first consider level of the incident light should be low such that $I_{ph} \ll I_0$. Under this condition

$$SPV \cong \frac{kT}{q} \frac{A\eta q\Phi_0(1-R)}{hv} \alpha, \quad (4.2)$$

where Φ_0 is the incident light intensity, R is reflectivity, η is the collection quantum efficiency, α is absorption coefficient, t is the QW thickness, A is the illuminated area and hv is the photon energy. Assuming that variation of R and η with photon energy can be neglected and Φ_0 is constant over the wavelengths of interest [26], we get

$$(hv) \times SPV(hv) \propto \alpha(hv). \quad (4.3)$$

Next, we observe that, there exists a connection between the numerical derivative of absorption coefficient and dielectric function differentials [12,13], similar to that valid for $\Delta R/R$ as mentioned in Section 1. This can be written as [27]

$$d\alpha(v) = \gamma(v)\Delta\varepsilon_1(v) + \delta(v)\Delta\varepsilon_2(v). \quad (4.4)$$

Therefore, a numerically differentiated quantity $d/d(hv)[hv \times SPV(hv)]$ is equivalent to Eq. (4.4) where $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are the respective changes in ε_1 and ε_2 at two nearby energy values. The resulting derivative spectrum is known to be equivalent to wavelength modulated reflectance modeled by first derivative Aspnes line shape function with $m=2$ [11,13]. We have used this formulation to obtain the transition energy values from the measured SPV spectra [24]. Fig. 3a shows the ER spectrum of the transition labeled e_1 - hh_1 and a calculated fit; using the Aspnes line shape function with $m=2$. Fig. 3b shows a numerically differentiated ($E \times SPV$) spectrum along with a calculated fit using the Aspnes line shape function with $m=2$. The values of E_0 from the two spectra agree fairly well.

5. Some applications

Applications of photoreflectance and electroreflectance techniques to (a) diffusion in QW [28], (b) electronic structure of self-assembled lateral superlattice [29] based on strain induced lateral ordering [30,31] and (c) linear electro optic effect [32] have been discussed in our earlier work. Here we shall detail some results of spectroscopic investigations of bulk and quantum structures using mainly surface photovoltage spectroscopy.

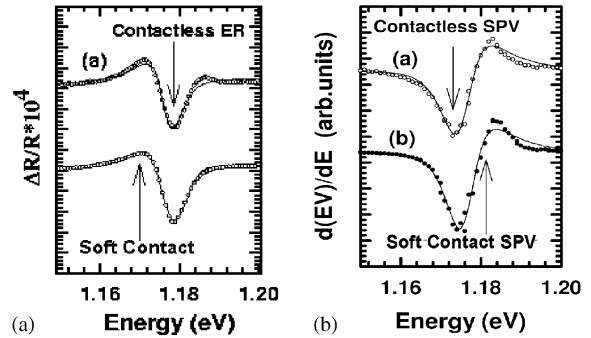


Fig. 3. (a) Comparison of ER and (b) derivative of SPV spectra of e_1 - hh_1 transition in contactless and soft contact mode for same sample as in Fig. 2. Dotted plots are measured data and continuous plots are the fits with Aspnes's line shape function with $m=2$.

5.1. SPV spectra of bulk n and p GaAs

Fig. 4 shows the spectra of (a) a bulk n GaAs sample and (b) a bulk p GaAs sample at room temperature. Band edge is seen clearly in both the spectra at the same energy. However, the magnitude of the SPV is very different for the two samples. The two spectra are measured under nearly identical conditions of incident light. The large difference in the magnitudes cannot be understood from the concept of static change in band bending. It can however be understood within the framework of the dynamic current balance model outlined above by noting the difference in the barrier height of the n- and p-type GaAs: ϕ_{bn} (~ 0.85 eV) and ϕ_{bp} (~ 0.6 eV). As a result I_0 for n-type sample is much smaller than I_0 for p-type sample resulting in considerably smaller SPV for p-type GaAs than for n GaAs.

5.2. Temperature dependence of the SPV magnitude of bulk GaAs

Fig. 5 shows temperature dependence of a bulk n-type GaAs sample excited with light at wavelength 750 nm, which is able to excite band to band electron-hole pairs with nearly the same efficiency over the entire temperature range. We see that the SPV magnitude decreases both above and below a certain transition temperature (~ 264 K for the sample under study). Conventional understanding of SPV resulting from photoinduced change in the band bending cannot explain this behavior. In line with our open circuit voltage model however, this form of behavior can be understood from temperature dependence of I_0 which generally has (i) a thermal component $I(\text{Th}) \sim I_{00} \exp(-\phi_b/k_B T)$ dominant at high temperatures and (ii) a relatively temperature independent component $I(\text{Nth})$ at low temperatures. We have applied the same model [18] to results of p-type

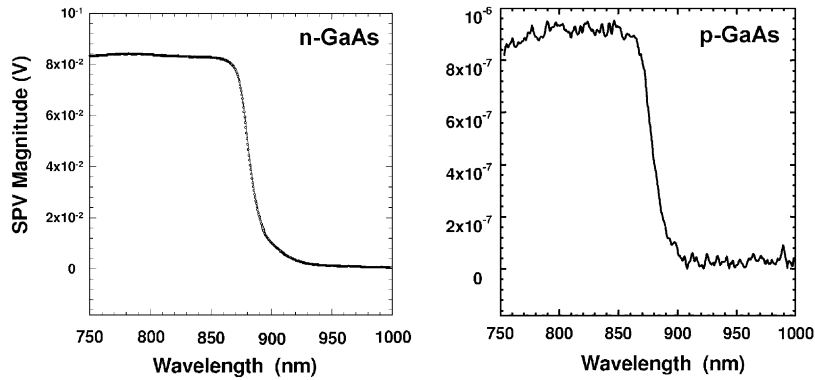


Fig. 4. Room temperature SPV spectra of bulk n- and p-type GaAs samples having similar doping concentrations ($n \sim 10^{16} \text{ cm}^{-3}$, $p \sim 2 \times 10^{16} \text{ cm}^{-3}$) recorded under similar conditions.

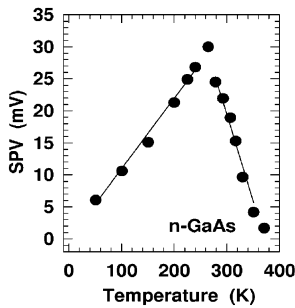


Fig. 5. Temperature dependence of SPV magnitude for an n-type bulk GaAs sample.

GaAs as well as n- and p-type InP with fair degree of agreement with the experimental behavior.

5.3. Temperature dependence of quantum well spectrum

Fig. 6 shows the SPV spectra of a 100 Å QW GaAs/In_{0.26}Ga_{0.74}As/GaAs at several temperatures over the range 150–27 K. As expected, the spectra shift to higher energy as the sample temperature is lowered. A surprising feature of the temperature dependent spectra is the shape near the e_1 - hh_1 transition as the sample temperature is lowered below ~ 100 K. There is an obvious loss of sharpness at lower temperatures. We find a similar broadening behavior for the QW e_1 - hh_1 transition from the electroreflectance measurements also. Peak nature of the spectrum at e_1 - hh_1 transition suggests the transition to be excitonic. It may be argued that the free exciton breaks up at high temperatures and contributes to I_{ph} , while below 100 K however, the exciton is unable to contribute to the photocurrent. An alternative plausibility is suggested by temperature dependence of the PL spectrum of the same sample which shows at low temperatures the PL spectrum consists of two features P_1 and P_2 separated by about

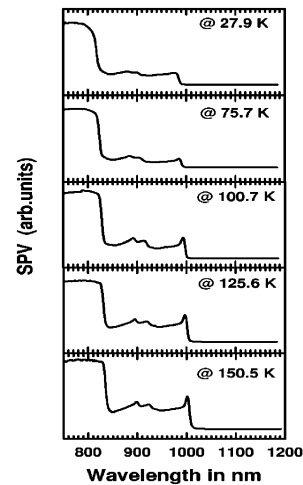


Fig. 6. SPV spectra of a GaAs/In_xGa_{1-x}As/GaAs single QW sample at different temperatures.

7 meV. We associate P_1 with free exciton transitions and P_2 with bound exciton transitions. Consistent with this assignment, we find magnitude of P_2 decreases with increase of sample temperature and disappears beyond 70 K. Since SPV broadening is also significant below 70 K, it is proposed [19] that the SPV broadening is also caused by the onset of the upward bound exciton transition. It is suggested that under field both free exciton and bound exciton break up and are able to contribute to I_{ph} . Above 100 K, the bound exciton transition does not exist, causing the line shape to become sharper both in the PL as well as in the SPV.

5.4. Quantum dots

Self-assembled quantum dot (QD) structures have been the subject of intense investigations. The growth mechanism known as Stranski–Krastronov [33,34]

depends heavily on the mismatch between the substrate and the material from which QDs are to be synthesized. For the first few monolayers, growth proceeds by 2D nucleation. These 2D nuclei grow and merge to form a smooth layer called wetting layer. If more material is deposited, the existing 2D nuclei transform into 3D islands or quantum dots [35]. Considerable effort has been made for exploring the synthesis of InAs or InGaAs QDs on GaAs. Lattice mismatch between InAs and GaAs is 7%. Even diode lasers incorporating InAs QDs as the active medium have been reported [36,37]. We have recently explored synthesis of InGaP quantum dots on GaP [38]. Fig. 7a shows smooth surface of epitaxially grown GaP. Fig. 7b shows surface which has deposition of thin planar layer of InGaP but it has not yet broken up into 3D islands. Fig. 7c shows a situation in which fairly high density of QDs ($\sim 10^{10}/\text{cm}^2$) have appeared. Fig. 8 shows a composite of SPV spectra taken at different growth stages. In the first stage (a) we see the SPV feature corresponding to only GaP below 550 nm. In the second stage (b) we see an additional feature due to the wetting layer at ~ 570 nm and in the third stage (c) we see also the feature due to the quantum dots peaking at $\lambda \sim 700$ nm. As such the signals corresponding to the wetting layer and the QDs are broad, indicative of size distribution. Changes in the wavelength of the part of the spectrum related to QDs and the corresponding line shape have also been observed as the mean size of QDs changes with the growth conditions [38]. The example thus shows SPV spectroscopy to be a powerful diagnostic tool for probing these nano-structures.

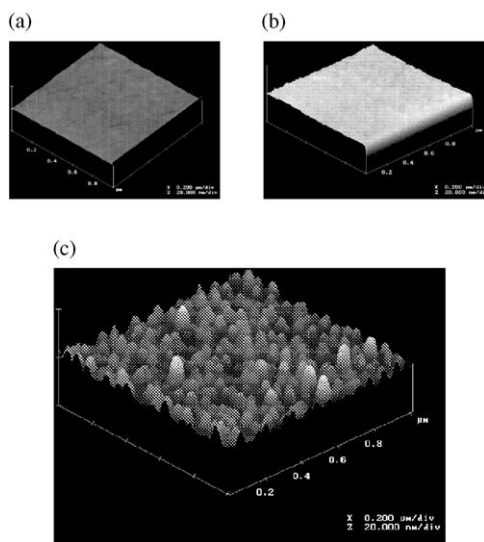


Fig. 7. AFM morphology of sample with (a) only GaP layer, (b) InGaP wetting layer on GaP and (c) InGaP quantum dots.

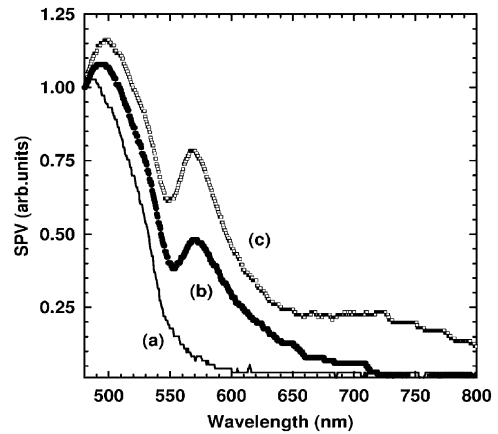


Fig. 8. SPV spectra of the samples whose morphology is shown in Fig. 7.

6. Summary

We have presented a brief account of recent developments in electroreflectance and surface photovoltage spectroscopies applicable to quantum structures. A few representative applications of surface photovoltage spectroscopy are also discussed.

Acknowledgements

Authors are thankful to several colleagues Prof. K.S. Chandrasekharan, Prof. K.L. Narasimhan, Dr. Arnab Bhattacharya, Mr. M.R. Gokhale, Mr. A.P. Shah, Mr. S.P. Pai, and Mr. Tarun Sharma of CAT, Indore for their participation and discussions in different aspects of the work presented here.

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