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Spectroscopy of systems with time variable parameters: photoreflectance of GaAs(001) under cesium adsorption

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Abstract

A modification of photoreflectance spectroscopy, which improves the precision and efficiency of measuring time-evolving surface electric fields, is proposed. This modification is explored for studying the band bending evolution under cesium adsorption on the reconstructed GaAs(001) surface and relaxation processes in the non-equilibrium adsorbate overlayer. Observation of several distinct maxima and minima in the coverage dependence of the band bending can be explained by the formation of adatom-induced surface states with a quasi-discrete spectrum.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Photoreflectance (PR) spectroscopy is widely used for the determination of built-in electric fields in various semiconductor structures. The magnitudes of the fields are determined from the period of Franz–Keldysh oscillations (FKO), which are observed in PR spectra for photon energies above the band gap [1, 2]. The facilities of PR spectroscopy are enhanced by phase-resolved detection of the spectra and by the Fourier-transform analysis of FKO [3, 4], which help to separate contributions originating from various regions of a layered structure with different built-in electric fields and to computerize the processing of the measured spectra. Being contactless, the PR technique is especially useful for studying semiconductor surfaces in ultra-high vacuum (UHV). PR spectra are highly sensitive to the adsorbates, which induce charged surface states and band bending. Therefore, extremely small concentrations (down to $\sim 10^{10}$ cm⁻² or $\sim 10^{-5}$ of a monolayer) of the charged adsorbates can be detected by means of PR spectroscopy, which are far smaller than the adsorbate concentrations determined by standard x-ray photoelectron or Auger spectroscopy techniques. The magnitude of the PR signal is proportional to the surface photovoltage (SPV). Thus, PR spectroscopy enables one to study the evolution of both the surface electric field and SPV. Reversible switching of the band

bending and SPV under alternate deposition of cesium and oxygen on the GaAs(001) surface proved the domination of the adatom-induced (rather than defect-induced) surface states at room temperature [5, 6]. PR spectroscopy also allowed us to trace the evolution of the electronic properties of a GaAs(Cs, O) photocathode during (Cs, O) activation to the state of negative electron affinity [7].

A typical problem of vacuum studies is that during spectral measurements the surface parameters, including the surface charge, vary in time due to the adsorption, desorption or relaxation processes in the adsorbate overlayer. These variations distort the measured spectra and, thus, limit the accuracy of the method. A possible solution consists in parallel acquisition of optical spectra by a linear array detector (photodiode array or CCD) at the exit position of a monochromator [8, 9]. However, parallel acquisition is not always suitable because of physical and technical reasons. A wide dynamic range of the measured signal is required for photoreflectance spectroscopy because, typically, PR signals are relatively small $\Delta R/R < 10^{-4}$. For parallel acquisition the dynamic range is restricted by the low capacity of a single CCD element and is usually below 10^4 for the accumulation time of about one second. The increase of the dynamic range by means of increasing accumulation time invalidates the advantages of parallel acquisition over the one-channel registration. It is also

difficult to combine the method of parallel acquisition with the lock-in detection technique, which yields a considerable enhancement of the signal-to-noise ratio. For PR spectroscopy an important drawback of using parallel acquisition consists also in the necessity to illuminate the sample with relatively high-intensity white light [9], in contrast to the low-intensity monochromatic illumination in the PR scheme with one-channel registration. High-intensity illumination induces a large surface photovoltage, which, in its turn, flattens the bands at the surface and causes a systematic error in the surface field and band bending determined from the period of FKO.

In this paper, we propose a new algorithm for one-channel spectral measurements, which enables us to increase the efficiency and accuracy of the determination of time-evolving parameters. Unlike the traditional measurements at fixed parameters, according to the proposed algorithm the spectra of a signal $f(\hbar\omega)$ are measured continuously, in the process of changing the system parameters. From the obtained array of signal values $f_i(\hbar\omega_i, t_i)$ measured at time moments t_i and photon energies $\hbar\omega_i$, the value of f at any given point $(\hbar\omega, t)$ can be determined by interpolation. By this interpolation it is possible to obtain spectra corresponding to the fixed values of time and, thus, to the fixed parameters.

The application of the proposed algorithm for studying the formation of the band bending φ_S at the Cs/GaAs(001) surface by PR spectroscopy allowed us to consider a long-standing problem related to the nature of electronic states at semiconductor surfaces with adsorbed metal overlayers [10, 11]. Specifically, under Cs deposition on the Ga-rich surface, we observed a nonmonotonic, consisting of several maxima and minima, dependence of φ_S on the adatom coverage θ . This ‘fine structure’ in $\varphi_S(\theta)$ occurs, supposedly, due to the formation of adatom-induced states with a quasi-discrete spectrum at the Cs/GaAs(001) interface. The relaxation from the non-equilibrium state of a Cs overlayer under Cs deposition to a quasi-equilibrium state after switching off the Cs flux is studied.

2. Experimental details

Epitaxial UP⁺ structures with thin (~100 nm) undoped i-GaAs surface layers grown on top of heavily doped p⁺-GaAs were used in order to provide a uniform electric field near the surface [2, 12]. The preparation of the clean As-rich and Ga-rich surfaces with various reconstructions included the removal of oxides in a solution of HCl in isopropyl alcohol (HCl-iPA) under a dry nitrogen atmosphere, transfer to the ultra-high vacuum (UHV) without air contact and subsequent annealing in vacuum [13, 14]. Cesium deposition was performed by using thoroughly outgassed dispensers. The dependence of Cs coverage versus deposition time was calibrated using x-ray photoelectron spectroscopy [15]. The band bending was calculated from the surface electric field, which was determined by the Fourier transform of the renormalized Franz–Keldysh oscillations [4, 16, 17].

Figure 1(a) shows a 3D illustration of the PR spectral measurements performed in a conventional experimental scheme at the clean GaAs(001) surface and at certain fixed

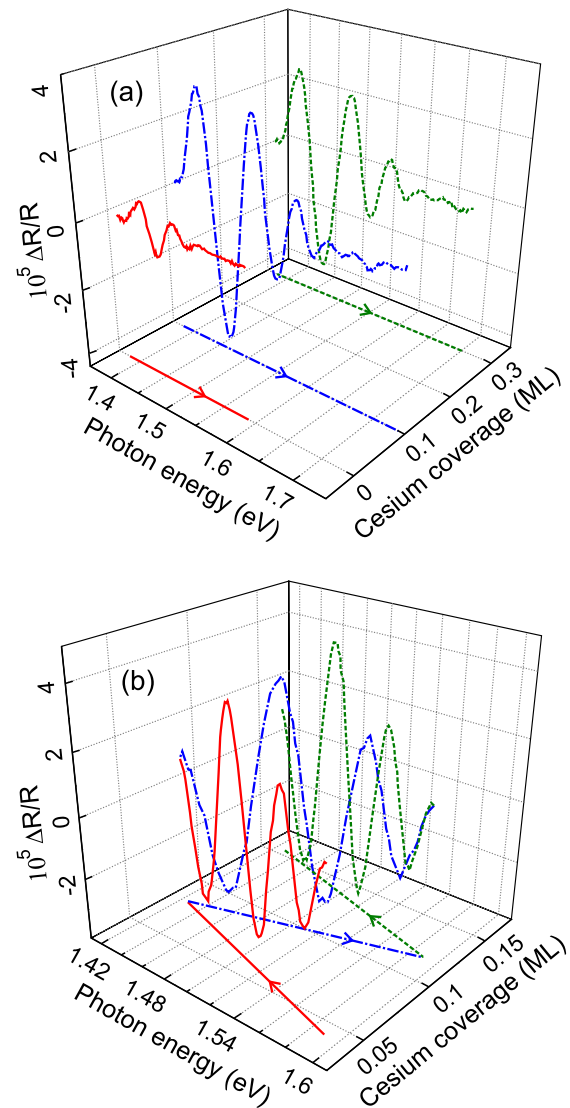


Figure 1. (a) Conventional photoreflectance spectroscopy: PR spectra measured at the clean GaAs(001) surface and at fixed Cs coverages θ ; (b) proposed algorithm for PR spectral measurements under continuous Cs deposition. The trajectories of photon energies $\hbar\omega$ and coverages θ during the measurements, which are shown by arrows in the $\hbar\omega$ - θ planes, illustrate the difference between the conventional and proposed algorithms.

cesium coverages θ . In each deposition, after switching the Cs flux off, the PR signal decreased by up to 50% with characteristic times of about 3–10 min and then saturated. It was proved experimentally that this decrease was not due to Cs desorption or to the influence of the residual atmosphere, but was caused, supposedly, by relaxation processes in the Cs overlayer. The amplitude of the decrease depended on the Cs coverage. The spectra were taken after the saturation of the PR signal, so that the error in the surface electric field caused by the spectrum distortion due to the signal drift was below 3%. Typically, the break between the end of Cs deposition and the start of the spectral measurement was about 5–20 min.

It is seen from figure 1(a) that Cs deposition leads to an increase of the FKO period, which corresponds to an increase of the surface electric field due to the formation and charging

of the Cs-induced donor-like surface states [6, 7, 18–20]. A simultaneous increase of the PR signal amplitude, which is also seen in figure 1(a), indicates the rise of the surface photovoltage under Cs deposition [21].

A drawback of the conventional algorithm is that the breaks in the measurements, which are necessary for depositing a successive adsorbate dose and allowing the interface to relax to a quasi-equilibrium state, are not used for the accumulation of the spectral data. The proposed new algorithm for the PR spectroscopy is illustrated in figure 1(b). According to this algorithm, PR spectra are measured continuously, under a constant flux of Cs, without breaks, one after another, in both directions of scanning, with a proper account for the backlash of the monochromator. Depending on the experimental condition, to acquire the necessary accuracy the measurement of each spectrum took from 2 to 5 min. Unlike the conventional algorithm, here the projection of the measured PR spectra on the $\hbar\omega$ - θ plane is a continuous zigzag line. PR spectra corresponding to certain points of time (and, thus, to fixed coverages) were obtained by linear interpolation of the experimental data array $\Delta R/R(\hbar\omega_i, t_i)$. The surface electric field F and band bending were determined by the Fourier transform of the interpolated spectra.

For the proposed modification of the PR technique, the accuracy of the electric field determination is determined, along with the random error of PR signal measurements, by the error of the interpolation scheme. In its turn, the interpolation error δF depends on the field variation ΔF during one spectrum scanning time and on the specific parameter dependence of the spectral shape. Franz–Keldysh oscillations are aperiodic: the period decreases with increasing photon energy [1], so the high-energy region of a spectrum corresponds to a smaller period and, therefore, is more sensitive to the magnitude of the electric field as compared to the low-energy region near the band gap. By the numerical simulation of the PR spectra [4, 16] obtained by the proposed algorithm, we proved that a linear interpolation yields a more accurate determination of the field for a pair of adjacent spectra with the common point at the high-energy end of the spectral region, as compared to a pair with the common point at the low-energy end. Specifically, in the former case the relative interpolation error $\delta F/F$ was below 2×10^{-3} for the values of $\Delta F/F$ up to ≈ 0.15 , while in the latter case $\delta F/F \approx \Delta F/F$.

3. Results

The dependencies $\varphi_S(\theta)$ measured by the conventional and new algorithms under Cs deposition on the Ga-rich surface of a MOCVD-grown GaAs(001) UP⁺ structure are shown in figure 2 by triangles and circles, respectively. It took more than 10 h to measure $\varphi_S(\theta)$ by the conventional algorithm. On the contrary, the new algorithm allowed us to obtain more data points and, thus, to measure the shape of $\varphi_S(\theta)$ with better precision during 3 h of continuous Cs deposition. Substantial contraction of the experimental run duration is also important for the minimization of the adverse influence of the residual atmosphere of the vacuum chamber on the surface with adsorbed cesium.

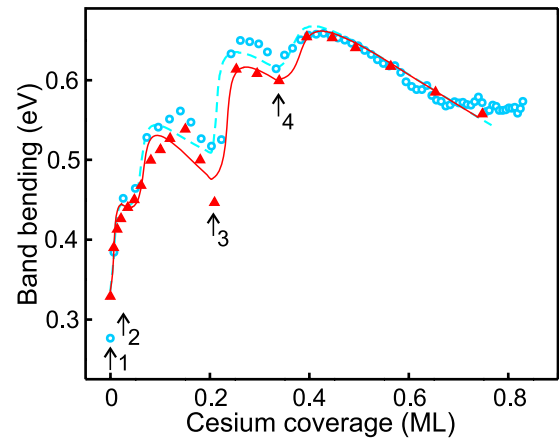


Figure 2. The coverage dependence of the band bending measured by the conventional algorithm, after relaxation of the adsorption layer at each Cs coverage from a non-equilibrium to a quasi-equilibrium state (triangles), and by the proposed algorithm under continuous Cs deposition on the Ga-rich GaAs(001) surface (circles). The solid and dashed curves represent the calculated dependencies for the quasi-equilibrium and non-equilibrium cases, respectively. The numbered arrows indicate threshold coverages for the onsets of the generation of the adatom-induced levels (see text).

It is seen from figure 2 that, in general, the measured dependencies are similar, although the new algorithm yields more detailed information about the shape of $\varphi_S(\theta)$. Several distinct maxima and minima are observed in the coverage dependence of the band bending. These maxima and minima were reproduced on the samples grown by both MBE and MOCVD techniques [22]. It is also seen from figure 2 that for $\theta < 0.45$ ML the values of band bending measured under continuous Cs deposition are larger by up to 20% than those measured by the conventional algorithm, with the Cs flux being switched off and the interface relaxed to its quasi-equilibrium state. With the help of the proposed new PR measurements algorithm, it is possible to measure not only the kinetics of the PR signal, but also the kinetics of the surface electric field and band bending during the relaxation of the Cs/GaAs interface from the non-equilibrium to the quasi-equilibrium state. The kinetics of the band bending was measured at various Cs coverages. To this end, the measurement of the PR spectra was continued after the coverage reached a given value and the Cs source was switched off. Applying the interpolation scheme described above to the measured ‘raw’ spectra, we calculated the PR spectra corresponding to fixed moments of time and, thus, determined the shape of the band bending kinetics during the relaxation of the interface to its quasi-equilibrium state. The resulting kinetic curves for four values of θ corresponding to the first maximum ($\theta = 0.15$ ML), to the first minimum (0.2 ML), and to the second and third maxima (0.3 ML and 0.45 ML, respectively) are shown in figure 3. For each θ , the band bending values φ_S were normalized to the corresponding initial value φ_0 , which was measured at the moment immediately before switching the Cs flux off. It is seen that the largest relative amplitude of the kinetics $\Delta\varphi_S/\varphi_0 \approx 18\%$ is observed at the first minimum of the band bending dose dependence $\varphi_S(\theta)$. The first and second maxima

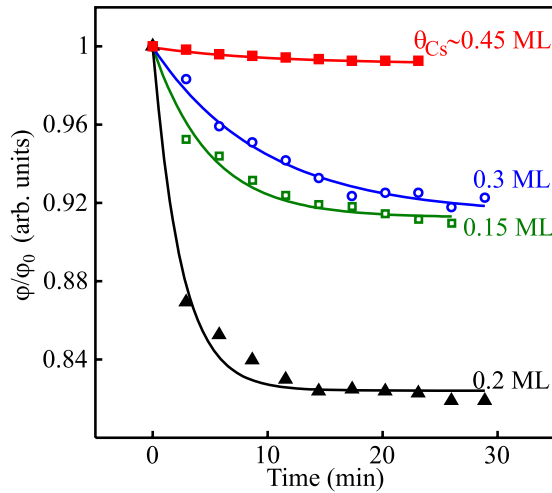


Figure 3. Relaxation of the band bending measured for various Cs coverages after switching off the Cs flux. The solid lines fit the experimental dependencies by simple exponential kinetics.

show $\sim 8\%$ kinetics. At coverages $\theta > 0.45$ ML the amplitude of the kinetics was less than 1%. Solid lines in figure 3 fit the experiment with simple exponential dependencies with characteristic decay times in the range of 3–10 min. The field relaxation times are close to the relaxation times of the PR signal, which is proportional to the surface photovoltage.

4. Discussion

To our knowledge, the ‘fine structure’ in $\varphi_S(\theta)$ (see figure 2), which consists of several maxima and minima, has not been observed before at adsorbate–semiconductor interfaces. The dose dependence with one maximum (so-called ‘overshoot’ behavior of the band bending) was observed earlier for alkali metal deposition on p-GaAs, and could be explained by the formation of a donor-like adatom-induced state in the band gap [10, 11, 18–20] rather than by defect-induced states [23]. Therefore, it may be supposed that the dependence with several maxima appears due to the formation of a set of adatom-induced levels. These levels may stem from consecutive filling of various adsorption sites on the reconstructed Ga-rich GaAs(001)-(4 × 2)/c(8 × 2) surface. It was shown in [15] and [12] that on the Ga-rich surface the adsorption of cesium occurs in a more ordered way as compared to the As-rich surface. Probably, this ordered adsorption is the reason for the pronounced ‘fine structure’ observed at the Ga-rich GaAs(001) surface. On the As-rich surface the dependence $\varphi_S(\theta)$ consists of one leading maximum (not shown) and is qualitatively similar to that observed earlier at the Cs/GaAs(110) interface [19, 20].

To prove these hypotheses and to determine the parameters of the adatom-induced surface states, the experimental data should be compared with theory. Unfortunately, there are no *ab initio* theoretical calculations which adequately describe the evolution of the band bending under an increasing concentration of adatoms at the Cs/GaAs(001) interface. We compared the results with a semiquantitative model by Klepeis

and Harrison [18], in which the effect of adatom-induced microdipoles on the energy of surface states was taken into account. The $\varphi_S(\theta)$ dependence calculated according to this model for the case of the quasi-equilibrium Cs/GaAs interface is shown in figure 2 by the solid line and closely describes the experiment shown by triangles. In the calculation it was assumed that, under Cs adsorption, four surface levels are successively generated in the band gap. Threshold coverages θ_i for the onsets of level generation are shown in figure 2 by the numbered arrows. The energy positions of the levels ε_i , the fractions of Cs adatoms ξ_i , which create each i th Cs-induced surface state, and the thresholds θ_i were used as fitting parameters. The fitted values of the energy levels lie in the range from 0.5 to 1.1 eV above the top of the valence band, and the fractions ξ_i are between 0.01 and 0.05. The shape of each peak is determined mainly by the parameters of the respective surface state. Therefore, despite the large number of fitting parameters, the values of the parameters are determined with a reasonable accuracy of about 10%–20%.

The smallness of the fractions ξ_i indicates that only a small part of Cs adatoms generates the high-energy levels, which determine the band bending evolution, while the major part of adatoms generates donor-like surface states which remain neutral because they lie below the Fermi level, i.e. in the lower part of the band gap and, probably, on the valence band background [24]. The non-homogeneous broadening of the surface states spectrum is a possible reason why, in the band gap of III–V semiconductors with submonolayers of alkali adatoms, it was not possible to observe photoemission lines corresponding to ionization of discrete adatom-induced states [11], with the exception of the Cs/GaP interface [25]. It should be noted that the model of discrete levels induced by individual Cs adatoms is not applicable for $\theta \geq 0.5$ ML, because for this region the adatom–adatom interaction leads to condensation of adatoms into two-dimensional islands with a metallic spectrum of electronic excitations [26, 27].

The kinetics of the PR signal and surface electric field after the Cs deposition is evidence of the formation of a non-equilibrium adsorption layer during Cs deposition. The kinetics observed after switching the Cs flux off is caused, supposedly, by the accommodation of the non-equilibrium Cs adatoms. This accommodation leads to a lowering of the surface states energy and band bending. To take into account the non-equilibrium state of the Cs adsorption layer, we calculated the $\varphi_S(\theta)$ dependence for the non-equilibrium adsorption by assuming that a certain fraction β of the deposited Cs adatoms occupy the adsorption sites which correspond to the next higher lying adatom-induced state. In figure 2, the dashed line shows the recalculated curve with the fitting parameter $\beta = 0.12$ and all other parameters the same as for the solid line, which describes the quasi-equilibrium occupation of the adsorption sites. It is seen that the dashed curve correctly describes the observed upward shift and the decrease of the ‘fine structure’ amplitude of the non-equilibrium $\varphi_S(\theta)$ dependence measured under continuous Cs deposition with respect to the quasi-equilibrium one. At large coverages $\theta > 0.45$ ML, when the transition from individual adatoms into 2D islands begins to occur [28],

virtually no kinetics was observed, probably due to fast condensation of incoming adatoms into the Cs islands. Thus, the observed kinetics is in accordance with the proposed hypothesis, although it is not possible to elucidate the details of the relaxation processes from the available experimental data.

5. Conclusions

In summary, we propose to improve the precision and efficiency of photorefectance spectroscopy for systems with time variable parameters by continuous spectral measurements during the evolution of the parameters, and subsequent extraction of the spectra corresponding to fixed parameters by the interpolation of the measured data array. Along with PR spectroscopy, the proposed algorithm of spectral measurements can be applied to other optical techniques as well. In particular, it is useful for monitoring the temperature of a GaAs slab, during heating and cooling in vacuum, by measuring the optical transmission or photoluminescence spectra in the near band gap region. The proposed modification of PR spectroscopy is applied to measuring the band bending evolution under cesium adsorption at the reconstructed GaAs(001) surface. Observation of several distinct maxima and minima in the coverage dependence of the band bending can be explained by the formation of a quasi-discrete spectrum of adatom-induced surface states. The observed kinetics of the PR signal and band bending prove the formation of a non-equilibrium Cs/GaAs(001) interface under deposition of cesium.

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