Contactless electromodulation for in situ characterization of semiconductor processing

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We present results of a new contactless electroreflectance (CER) mode which has considerable potential for in situ monitoring. This method utilizes a condenser-like system, one electrode consisting of a transparent conductive coating on a transparent substrate which is separated from the sample surface by a thin layer of air (or other ambient). In order to demonstrate the utility of this approach we have measured the CER spectra from (a) bulk $Hg_{0.8}Cd_{0.2}Te$ (80 and 300 K) sputtered with Xe ions as well as (b) (001) n- and p-type GaAs structures with large, uniform electric fields. The latter configurations can be used to investigate Fermi level pinning effects and metallization. Studies were carried out as a function of temperature ($10 < T < 600$ K) yielding a temperature dependence of surface barrier height. The relative merits of CER and photoreflectance will be discussed.

1. Introduction

Of the many optical methods used to investigate semiconductors and semiconductor microstructures, one of the most useful is electromodulation (EM) [1–3]. Until recently this modulation method could be performed in a contactless way by photoreflectance (PR) [2,3] or electron-beam electroreflectance (EBER) [4]. Furthermore, Gal and Shwe have reported a new version of differential reflectivity (contactless) which sometimes contains an EM component [5]. Recently Yin et al. [6–8] have presented a new contactless electroreflectance (CER) approach which utilizes a condenser-like system consisting of a wire mesh or thin, transparent, conductive coating (indium–tin–oxide or 5–6 nm of a metal such as Au or Ni) on a transparent substrate (glass, quartz, etc.) which serves as one electrode. A second electrode consisting of a metal strip is separated from the first electrode by insulating spacers. The sample (~ 0.5 mm thick) is placed between these two capacitor plates. The dimen-

sions of the spacer are such that there is a very thin layer (~ 0.1 mm) of air (or vacuum) between the front surface of the sample and the conducting part of the first electrode. Thus, there is nothing in direct contact with the front surface of the sample. The AC modulating (~ 1 kV peak-to-peak) and DC bias voltages are applied between the metal strip and the transparent front electrode. Contactless electroreflectance is thus a majority carrier effect. The probe beam is incident through the first transparent electrode. This technique is not only contactless but can be used in any transparent medium, including air or vacuum. This approach also can be employed in the transmission mode by replacing the metal electrode with a second transparent electrode/substrate.

In addition, this technique has some advantages over PR: (a) because CER is a majority carrier effect it can be performed more conveniently at high temperatures (> 400 K) in relation to PR [8], (b) CER yields signals at 300 K in narrow-gap semiconductors such as $Hg_{1-x}Cd_xTe$
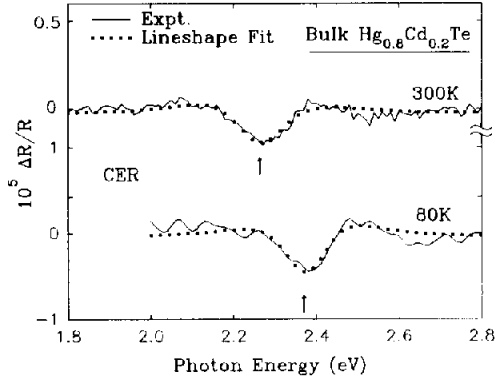
Fig. 1. CER spectra (solid lines) at 300 and 80 K from bulk Hg$_{0.8}$Cd$_{0.2}$Te sputtered with Xe ions. The dotted lines are least-squares fits to a TDFF lineshape.

($x \approx 0.2$) [6,8], (c) the phase of the CER signal yields information about the nature of the band bending at the surface of bulk or epitaxial material [7], and (d) there is no photoluminescence effect in CER measurements.

In this paper we present some recent results that demonstrate the considerable potential of this method for in situ applications. This work includes CER measurements of (a) bulk Hg$_{0.8}$Cd$_{0.2}$Te (80 and 300 K) sputtered with Xe ions and (b) (001) n- and p-type GaAs structures with large, uniform electric fields. These latter configurations can be used to investigate Fermi level pinning effects and metallization. Studies were carried out as a function of temperature ($10 < T < 600$ K) yielding the temperature dependence of the surface barrier heights.

2. Experimental results and discussion

Shown in the upper part of fig. 1 is the CER spectrum at 300 K (solid line) of a bulk Hg$_{0.8}$Cd$_{0.2}$Te sample in the range of the E_1 feature ($\Lambda_3-\Lambda_1$ transitions in the Brillouin zone) after sputtering with 1.0 keV Xe ions. The CER measurements were obtained using a modulating voltage of 500 V at 200 Hz. No PR signal at 300 K could be obtained from this narrow-band-gap material. The dotted line is a least-squares fit to a third-derivative functional form (TDFF) line-

shape for a two-dimensional critical point [1]. This procedure yields the energy of the transition, as indicated by the arrow at the bottom of the figure, and the linewidth (Γ). The energy at 300 K makes it possible to determine the Hg composition [2]. The parameter Γ (160 meV) yields information about the quality of the crystal, i.e., process-induced damage [9]. These results are extremely significant since in the past it has not been possible to obtain signals from Hg$_{1-x}$Cd$_x$Te ($x \approx 0.2$–0.3) at 300 K using other contactless EM methods such as PR or EBER. These experimental techniques have yielded signals only at 77 K or below [4,10]. The material Hg$_{1-x}$Cd$_x$Te ($x \approx 0.2$–0.3) is extremely useful for infrared detectors.

In order to determine the effects of thermal broadening on Γ we also have performed the CER experiment at 80 K. These results (solid line) are displayed in the bottom of fig. 1. Again the dotted line is a fit to a TDFF which yields the energy indicated by the arrow and $\Gamma = 140$ meV. Such a linewidth is considerably larger than those that would be expected from undamaged material. For example, at 77 K using PR for the E_1 feature of CdTe $\Gamma = 63$ meV [11] while for Hg$_{1-x}$Cd$_x$Te of a somewhat higher composition ($x = 0.3$) $\Gamma = 80$ meV has been reported [10]. Undamaged Hg$_{0.8}$Cd$_{0.2}$Te should thus have $\Gamma \approx$ 70–75 meV. Thus the large Γ for this sample at 80 K is due to the effects of the Xe-ion sputtering.

We also have investigated CER and PR from (001) n- and p-type GaAs structures with large, uniform built-in electric fields [12–15] as a function of temperature. These configurations, designated UN$^+$/UP$^+$, have been extremely useful in investigating surface/interface Fermi level pinning [12–17]. The signals from such samples exhibit a large number of Franz–Keldysh oscillations (FKO) originating in the large, almost uniform field created by the Fermi level pinning. Furthermore, because of strongly temperature-dependent surface photovoltage effects, $V_s(T)$, in both PR (probe and pump beam) and CER (probe beam) the field evaluated from the FKO is not a direct measure of the Fermi level pinning position, V_F, but rather the surface barrier height, V_B

$(= V_F - V_S)$. This problem can be overcome by performing the experiment at elevated temperatures (> 400 K) [13–15]. In this temperature range the photovoltage effect is eliminated because of the enhanced saturation (or dark) current [13–15]. However, it is then not possible to modulate the bands by the pump beam (photovoltaic effect) and the minority carrier PR signal disappears [8,13–15]. Because CER is a majority carrier effect it is still possible to obtain spectra at $T > 400$ K [8].

Shown in fig. 2a are the CER (solid curve) and PR (dashed curve) data from the UN^+ sample at 300 K. The PR signal is about twice as strong as the CER trace. The 500 K results are shown in fig. 2b. The PR spectrum is now about an order of magnitude smaller and exhibits fewer FKO in relation to the CER signal.

In order to study the temperature dependence of Fermi level pinning we have performed CER on bare (in air) and metallized (5 nm Au) UN^+/UP^+ samples in the range $10 < T < 600$ K. Shown in fig. 3 by the open circles and squares are V_B for bare UN^+ and UP^-, respectively, in this temperature regime. The curves for the bare UN^+/UP^+ structures exhibited no hysteresis with temperature cycling in the entire range. Below about 450 K these results are similar to those
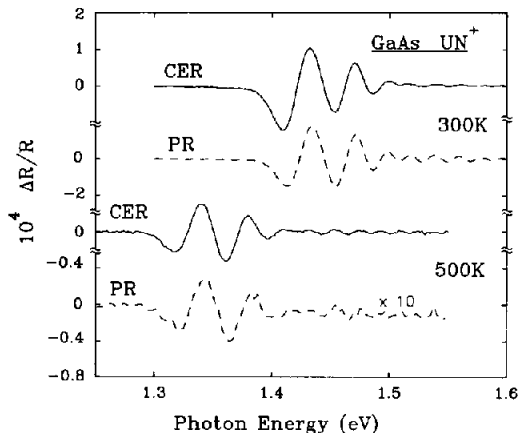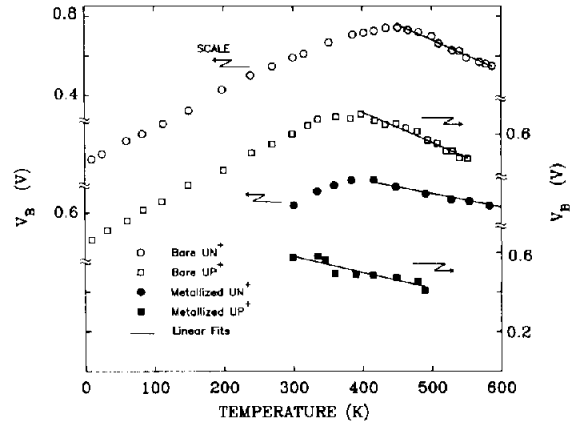

Fig. 3. Measured barrier height V_B, as a function of temperature, for bare and metallized UN^+ and UP^+ samples. The solid lines are least-squares fits to a linear function.

Fig. 2. CER and PR spectra from a UN^+ sample at 300 and 500 K.

previously reported using PR [13–15]. The measured barrier increases with higher temperature because $V_s(T)$ is diminished. Above about 450 K $V_s(T)$ is essentially zero and so V_B is a direct measure of V_F, which also has a temperature dependence. Above 450 K V_B begins to decrease with higher temperature because of $V_F(T)$. The solid lines are least-squares fits to a linear function yielding temperature coefficients (α) of V_F. For the UN^+ and UP^+ bare surfaces $\alpha_b(n) = (1.5 \pm 0.2) \times 10^{-3}$ eV/K and $\alpha_b(p) = (1.5 \pm 0.2) \times 10^{-3} \times 10^{-3}$ eV/K, respectively. These values are considerably larger than the linear temperature exponent for bulk GaAs ($= 5.1 \pm 0.5 \times 10^{-4}$ eV/K) [18].

The results for the metallized UN^+/UP^+ samples are displayed by the solid circles and squares, respectively, in fig. 3. Again the solid lines are least-squares fits yielding $\alpha_m(n) = (6.6 \pm 1.4) \times 10^{-4}$ eV/K and $\alpha_m(p) = (7.7 \pm 2.1) \times 10^{-4}$ eV/K for the metallized UN^+ and UP^+ structures, respectively. These results are comparable to the temperature coefficient of the GaAs band gap.

We offer the following tentative explanation of our results. First, for the bare structures we believe that the discrepancy between the actual temperature coefficients above 450 K and the coefficient for the bulk band gap of GaAs can be

explained in terms of "unpinning" the Fermi level at elevated temperatures. It is well known that the equilibrium species at air-exposed GaAs interfaces include: Ga_2O_3, As_2O_3, and elemental arsenic [19]. It is also well known that Fermi level pinning at GaAs surfaces and interfaces is associated with the presence of excess As. Furthermore, photowashed GaAs which is free of excess As and arsenic oxide is unpinned and the remaining gallium oxide acts as a weak barrier to the reforming of the arsenic species, and, hence, repinning, in air [19]. Therefore, we suppose that during the heating and cooling cycle above 450 K in air, the high vapor pressure arsenic species are driven off faster than they are reformed in air, thus reducing the effective surface state density. Upon cooling below 450 K in air the pinning species reform faster than they are driven off. This notion is consistent with the fact that the metallized structures show the expected behavior with temperature, indicating that the pinning species are trapped at the interface during the heating and cooling cycle. Further work needs to be done to confirm this conjecture.

3. Conclusions

In conclusion, we have presented results of a new contactless form of EM which has considerable potential for in situ monitoring. This method employs a capacitor-like system. The utility of this approach has been demonstrated by measuring the CER spectra from bulk $Hg_{0.8}Cd_{0.2}Te$ (80 and 300 K) sputtered with Xe ions and (001) n- and p-type GaAs structures with large, uniform electric fields. The latter configurations have been investigated as a function of temperature ($10 < T < 600$ K) yielding a temperature dependence of the Fermi pinning level. Since CER is a majority carrier effect it can be used in situations where PR is not applicable such as small-gap materials at 300 K and UN^-/UP^+ structures at elevated temperatures. Also, the phase of the CER signal can be used to determine the carrier type.

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