Photomodulation raman spectroscopy as a pump-probe technique for surfaces and interfaces of semiconductors

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Abstract. Photomodulation Raman spectroscopy (PM-RS) has been employed to study the surface depletion electric field $E_s$ and to monitor the change in surface charge density in n-type GaAs, using the forbidden LO phonon scattering for low doping samples and coupled plasmon–LO phonon modes for high doping samples. In PM-RS, the photomodulating pumping beam (PB) is incident on the sample while the Raman measurements are in progress hence PM-RS can be viewed as a pump-probe technique. The photogenerated carriers partly neutralize the surface charges. Two different GaAs surfaces (011) with low and moderate doping density and (001) with high doping density were used. The total surface charge density has been obtained as a function of the PB intensity considering a constant depletion electric field for the lower doping sample of (011) surface and using the dependence of the unscreened LO phonon on the depletion width for the higher doping samples of (001) surface. The minority carrier’s lifetime was also determined through dynamical measurements for the PM-RS of the low doping sample as $\approx 21$ s, in a good agreement with other techniques.

1. Introduction
Photomodulation Raman Scattering (PM-RS) is a relatively new pump-probe technique [1,2] which is used to study the variations of the electric field ($E_s$) inside the surface depletion region of doped semiconductors and surface charge densities. This depletion electric field $E_s$ induces forbidden LO phonon Raman scattering (EI-RS [3]) due to modification of the polarization selection rules in the depletion region. The intensity of
this EI-RS signal is a direct measure of $E_s$ and hence it can be used as a sensitive microscopic probe for detecting any perturbation of $E_s$ at semiconductor surfaces. In PM-RS experiments, the pump beam (PB) of energy larger than the band gap of the material perturbs the depletion field at the semiconductor surfaces while the probe beam measures the EI-RS signal to detect this perturbation. The microscopic mechanism of the technique can be described as follows. The pump beam creates electrons and holes within its whole penetration depth ($\delta_{PB}$). The created carriers within the depletion region are separated by the built-in field, and partly neutralize the surface charges. This in turn decreases the depletion electric field $E_s$ and leads to a decrease in the intensity of the EI-RS. Also, the reduction of the surface charge density with photoexcited carriers leads to a decrease in the depletion width ($L$), thus affecting EI-RS from the depletion region when $L < \delta_R$ (the penetration depth of the Raman probe beam). For highly doped semiconductors where the condition of $L < \delta_R$ is verified, the pump beam affects both $E_s$ and the scattering length (which is limited to $L$).

In highly doped polar crystals, the plasma oscillation and the bulk LO phonons couple via their macroscopic electric fields [4]. To observe these coupled modes, $\delta_R$ must be larger than $L$ (which represents an important parameter for these measurements). The Raman signal in this case carries surface unscreened LO information (in the depletion region) and bulk information (the coupled LO-plasmon modes). The Raman signal in these measurements is less affected by the surface field, but it is sensitive to any change in the depletion width $L$, which controls the scattering length of the unscreened LO and the coupled modes. These measurements can allow the experimental separation of the impact of the surface electric fields from the effect of the depletion width on the Raman signals. Hence one can separate the effect of the pumping process on $E_s$ from that on the depletion width.

In this work we used PM-RS to affect the depletion field and consequently the depletion width for (011) n-type GaAs single crystals. The intensity of the forbidden LO was measured as a function of the intensity of the PMB. Also PM-RS has been applied to the LO-plasma coupling for the (001) surface of an n-type GaAs single crystal. In this case the allowed unscreened LO depends mostly on the depletion width $L$ and is observed in cross-polarization configuration. On the other hand, the EIRS (forbidden LO) depends on both the surface field $E_s$ and the depletion width $L$ (as a scattering length and is observed in parallel-polarization configuration). By comparing the resulting PM-RS of the forbidden LO to the allowed LO, we are able to separate the effect of the PB on the depletion width from its effect on the surface field. Furthermore, the present experiments provide dynamic measurement of the Raman scattering intensity by following the increase in the intensity of the forbidden LO after the pump beam is turned off. Using this technique we were able to calculate the surface state (trap) discharging time through a simple carrier recombination and generation model. The resulting values are in a good agreement with other measurements using more demanding techniques (e.g. photomodulation second harmonic generation). This combined PM-RS technique provides a dynamic non-contact, non-destructive method to vary the surface field $E_s$ and measure interfacial electronic properties of semiconducting materials.
2. Experimental

The samples studied were n-type GaAs of two different surfaces (011) and (001). The doping densities used for the first surface are \((7 \times 10^{15} \text{ cm}^{-3} \text{ with } L \approx 0.4 \mu\text{m} \text{ and } 2.3 \times 10^{17} \text{ cm}^{-3} \text{ with } L \approx 780 \text{ Å})\) and \((5.8 \times 10^{17} \text{ cm}^{-3} \text{ with } L \approx 500 \text{ Å} \text{ and } 1.1 \times 10^{18} \text{ cm}^{-3} \text{ with } L \approx 260 \text{ Å})\) for the second surface. The forbidden LO scattering intensities were measured in the parallel configuration with the polarization of the incoming and scattered photons along [100] direction. The spectra have been normalized using the TO as an internal reference for (011) surface. The intensity of the incident light (probe beam) from Ar⁺ laser at \(\lambda_R = 4880 \text{ Å}\) beam \((2.54 \text{ eV})\) was \(15 \text{ W cm}^{-2}\) (at the sample). The pump beam was incident on the samples at the same time and was carefully aligned on the same scattering spot in all the experiments. This arrangement gave us the best experimental conditions to observe the effect of modulation of the band bending. In all the experiments each recorded spectrum is an average of at least five measurements. The surface quality is essential, since surface damage and contamination may cause a shift and broadening of the coupled mode from (001) surface [5]. For the two samples of this surface, the Raman penetration depth, \(\delta_R\), is larger than the depletion width for all wavelengths used, which allows observation of the coupled plasmon modes. The values of the depletion widths quoted above were taken from [6]. The penetration depths for all wavelengths used in this work were calculated from \(\delta = \frac{l}{4\pi\kappa}\), using the available data for the extinction coefficient \(\kappa\) of GaAs [7].

3. Results and Discussion

The PM-RS spectra obtained at an intensity 15 W cm\(^{-2}\) for the pump beam (at the sample) comparable to the intensity of the probe beam, are shown in Fig. 1. The pump beam is off for (a, c) and on for (b, d) using \(\lambda_{pb} = 4579 \text{ Å}^\circ\), with \(\delta_{pb} (<700 \text{ Å}^\circ)\) falls within the depletion region for both samples. It can be seen from these results that there is a decrease in the forbidden LO phonon scattering intensity in the two samples relative to their intensities in the absence of the pump beam. However, the decrease for the higher doped sample, is almost 32%, while for the other sample with lower doping, the decrease is only 21%. It should be mentioned that the difference in the decrease of the LO scattering intensity for the two samples is due to the fact that the signal in the higher doped sample is more sensitive to the pump beam because of the decrease in both of the depletion field strength and the scattering length which is limited to \(L\), when \((L < \delta_R)\). On the other hand for the sample with low doping (that has much larger depletion width \((L > \delta_R)\) the effect is due only to the decrease in the field since the scattering is coming only from \(\delta_R\). Assuming a constant field approximation (when \(L \) is large compared to the distance that is optically probed), the near surface depletion electric field can be written as \(E_o = 2\pi\sigma_o/e\); where \(\sigma_o\) is the surface carrier density.

When the pump beam illuminates the sample long enough for the carrier populations to reach steady state, the surface charge density \(\sigma_o\) (majority carrier) is reduced by a factor of \(p_o\), which is the surface minority carriers density generated by the pump beam The electric field \(E_{on}\) with the pump beam on, is accordingly related to \(E_o\) by \(E_{on} = E_o \sigma/e\sigma_o\); where \(\sigma = (\sigma_o - p_o)\) is the net surface charge density. Since the forbidden LO scattering intensity is proportional to \(E_o^2\), the ratio of the PM LO scattering intensity to that in the absence of the pump beam is then given by \(I/I_o = (E_{on}/E_o)^2 = (\sigma/e\sigma_o)^2\). This relation can also
be used to determine the change in the surface carriers density as a function of the pump beam intensity $I_{PB}$. The total surface charge density $\sigma$ as a function of $I_{PB}$, is shown in Fig. (2) for the sample of low doping density, where $|\sigma| = 3.22 \times 10^{11}$ cm$^{-2}$: In the case of the high doping sample, the assumption of constant depletion electric field is not valid ($\delta_R > L$) hence the calculation of the surface charge density could not as easily be obtained. Furthermore, since the total surface charge density is $|\sigma| = N_eL$; due to charge neutrality, changing $I_{PB}$ from 0 to 50 W cm$^{-2}$ results in a change in the depletion width from about 0.46 µm [6] to 0.34 ± 0.007 µm.

The PM-RS results for the sample with doping density $1.1 \times 10^{16}$ cm$^{-3}$, using $\lambda_R = 4579$ Å and PB of $\lambda_{PB} = 4880$ Å at three different intensities $I_{PB}$ (20, 30 and 40 W cm$^{-2}$), are shown in Fig. 3, together with the case without a PB. The spectra were obtained at room temperature in the cross-polarization $z(xy)z$ configuration and the intensities of the PB were measured at the surface of the sample. In these experiments, carriers were generated inside as well as outside the depletion region, $L$, for both samples, since $\delta_{PB} > L$ in both cases. It is observed that, with increasing $I_{PB}$, the scattering intensity of the coupled modes increases without a change in the frequency shift, while that of the unscreened LO phonon decreases.

The same observations hold for the other sample with doping density $5.8 \times 10^{17}$ cm$^{-3}$ under the same conditions. These results could be explained according to the fact that the reduction in the depletion width is a direct result of the decrease in the surface charge density resulting from PB. This is reflected as a decrease in the scattering length for the unscreened LO mode and at the same time an increase in the scattering length for the coupled modes. The intensity of the unscreened LO phonon, $I_{LO}$, within the depletion region is proportional (to a first-order approximation) to $L/\delta_R$ [8].
Figure 3. PM-RS spectra of n-GaAs (1.1 × 10^{18} \text{ cm}^{-3}) in the cross-polarization configuration from the (001) surface at three different values of $I_{PB}$ (as indicated) and with no PB.

Figure 4. The normalized intensity $I_{on}/I_{off}$ of the allowed and forbidden LO phonons for n-GaAs (5.8 × 10^{17} \text{ cm}^{-3}) as a function of $I_{PB}$. The variation of $E_{on}/E_{off}$ as a function of $I_{PB}$ is shown in the inset.

Consequently, $(I_{on}/I_{off})_{LO} = L_{on}/L_{off}$ at constant $\delta_R$ and, since $\sigma = N_eL$, we may write $\sigma = \sigma_0(I_{on}/I_{off})$. This relation is used to determine the change in the surface carrier density as a function of the PB intensity. Accordingly, the total surface charge density $\sigma (N_e = 5.8 \times 10^{17}\cm^{-3})$ changes from $2.9 \times 10^{12}\cm^{-2}$ (the value of $\sigma_0$) to $(1.92 \pm 0.038) \times 10^{12}\cm^{-2}$, while $\sigma (N_e = 1.1 \times 10^{18}\cm^{-3})$ changes from $3.9 \times 10^{12}\cm^{-2}$ to $(2.77 \pm 0.055) \times 10^{12}\cm^{-2}$ on changing $I_{PB}$ from 0 to 50 W cm^{-2}.

To compare the above results with the effect of the PB on field-induced LO phonon, Fig.4 shows the normalized intensity of the allowed LO, $I_A (=E_{on}/E_{off})$, together with that of the forbidden LO, $I_F (=E_{on}/E_{off})$, as a function of $I_{PB}$, for the sample of $N_e = 5.8 \times 10^{17}\cm^{-3}$ where $E_{on}$ and $E_{off}$ are the values of $E_s$ with the PB on and off, respectively. These results reflect a stronger effect of the PB on the intensity of the forbidden LO that is proportional to the square of the surface field $(E_s^2)$ in addition to the depletion width $L$ as a scattering length $(L < \delta_R)$ as was mentioned earlier. The above comparison shows that the variations in the surface field as a function of $I_{PB}$ can be extracted (separated) and calculated simply using the following relation:

$E_{on}/E_{off} = (I_F/I_A)^{1/2}$

which is presented in the inset of figure 4. These results show the ability of the PM process to decrease the surface field to about 73% of its original value at the largest intensity used for PB (50 W cm^{-2}), which illustrates the success of this process in affecting significantly the surface charges even for such highly doping samples.

The intrinsic free minority carriers has a small density compared with the photoexcited minority carriers and can be ignored, hence the rate of the decay of the minority carrier density after the pump beam is turned off can be written as $d\rho(t)/dt = -\rho(t)/\tau$ [6] where $\tau$
represents the surface minority carrier’s lifetime. With the boundary condition \( p(t=0) = p_0 \) we get \( p(t) = p_0 e^{-t/\tau} \). Consequently the time dependent intensity ratio \( I(t)/I_0 \) after the pump beam is turned off at \( t = 0 \) has the form \( I(t)/I_0 = (1 - p_0 e^{-t/\tau})/\sigma_0 \).

In our time-dependent measurements, we recorded the increase in LO scattering intensity after the pump beam is turned off. This is a direct measurement of the surface state (trap) discharging time. The measurements were carried out by illuminating the sample for at least 2 min then the PB beam shutter was closed and the LO scattering intensity was monitored as a function of time. This procedure was repeated about 50 times. A typical time dependent LO Raman scattering of our lowest doping sample for the discharging case, is plotted as a function of time in Fig. 5. The solid line is our best fit to the experimental results based on the above model. The calculated discharging time is \( t = 21 \pm 1.25 \) s. This result is in agreement with other measurements, e.g. that was given by Qi et al. [9] using photomodulation second harmonic generation.

Microscopically, the minority carriers photoexcited within the depletion region drift to the surface, and are trapped quickly by interfacial defects in a time \( t_c \) \((10^{-6} \text{ to } 10^{-10} \) s) [10]. The trapped photoexcited minority carriers has such a long lifetime at the surface due to the fact that the depletion field separates electrons and holes in space. Furthermore, before recombining and leaving the surface, these carriers can be excited thermally from the traps into free carrier states near the surface that diffuse along the surface until they become trapped again. This process may be repeated many times before the recombination of the carriers takes place. Namely, there is a substantial amount of trap excitation/deexcitation during the carrier lifetime.

![Figure 5](image-url)

**Figure 5.** The normalized intensity \( I(t)/I_0 \) for n-type \( 7 \times 10^{15} \) cm\(^{-2} \) GaAs as a function of time after PB light was turned off.
4. Conclusion

we have shown that the pumping light has significantly modulated the surface EI-RS and the coupled plasmon–LO phonon of GaAs. we were able to calculate the net surface charge density as a function of PB intensity. Also, this process helps us to differentiate the effect of PB on the depletion field strength from the effect on the depletion width. Furthermore we were able to calculate the surface trap lifetime for the low doping sample using a simple model for carrier recombination and generation. The success of these experiments suggest that this technique has the potential to be a useful non-contact probe of interfacial electronic properties which in turn may help us to design better electronic devices.

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