

Experimental detection and control of trions and Fermi edge singularity in single barrier GaAs/AlAs/GaAs heterostructure using photocapacitance spectroscopy

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Abstract

In this paper, we show how photocapacitance spectra can probe and manipulate two dimensional excitonic complexes and Fermi edge singularity as a function of applied bias even at a temperature of 100 K. For lower density regimes ($<1 \times 10^{11} \text{ cm}^{-2}$), appearance of two distinct peaks in the spectra are identified as a signature of coexistence of both excitons and positively charged trions. We found the binding energy of these trions as $\sim 2.0 \text{ meV}$ which matches well with known estimates. For higher density regimes ($> 1 \times 10^{11} \text{ cm}^{-2}$), we observe a sharp spectral transition from trions to asymmetrically shaped Fermi edge singularity in photocapacitance spectra above a particular reverse bias. However, these signatures of indirect excitonic states were absent from photoluminescence spectra. Such dissimilarities clearly point out that different many body physics govern these two spectral measurements. We also argue why such quantum confined dipoles of spatially indirect trions can have thermodynamically finite probability to survive even around 100 K. Finally, our observations demonstrate that photocapacitance spectroscopy, which was hardly used to detect trions in the past, can also be useful to detect the traces of these spatially indirect excitonic complexes as well as Fermi edge singularity. This is mainly due to enhanced sensitivity of such capacitive measurements to ‘dipolar’ changes of excitonic complexes in these heterojunctions. Thus, our studies clearly open up future possibilities for electro-optical modulation and detection of trions and Fermi edge singularities in several other heterostructures for next generation optoelectronic applications.

I. INTRODUCTION

Experimental study of neutral excitons (say X^0) and charged excitons like positively or negatively charged trions (X^+ or X^-) inside two dimensional (2D) semiconductor quantum structures are becoming important for understanding the many body physics of excitonic complexes [1,2] as well as for novel applications of excitonic devices [3]. Existence of trions was first demonstrated in semiconductors by Lampert [4]. Since then, there are numerous reports on the optical spectroscopic signatures of trions at low temperatures of few Kelvins. This is mainly because of small binding energies ($\sim 1-2$ mV) of trions in III-V material system [5-7]. Whereas, trions in 2D monolayers of transition metal di-chalcogenides (TMDC) can have much larger binding energies [8,9] $\sim 20-50$ meV. Such large binding energies of excitons and trions in TMDC materials can certainly make it much easier, not only to study the many body physics of excitonic complexes even at room temperature, but also for their use in optoelectronic devices. However, there are also reports of some disparities between theoretical and experimental observations of precise signature of positively or negatively charged trions and their expected binding energies [7]. According to theoretical predictions [10], binding energy of positively charged trions should be higher due to larger hole effective mass but experiments had reported nearly similar values of binding energies [11] for both X^+ and X^- . At this point, we understand that identifying a trion as X^+ or X^- depends mostly upon how electrons and holes are being injected with applied bias based on the device configuration. The presence of these excitonic complexes usually occurs in moderate density regimes. Whereas many body interactions of charge carriers with Fermi sea lead to Fermi edge singularity (FES) in high density regimes. This was first predicted by Mahan [12] in degenerate semiconductors. Theory [13,14] and experiments [15-17] of such crossover to FES in III-V semiconductors were studied mostly at

low temperatures of few Kelvins by optical absorption and photoluminescence (PL) spectroscopies.

In the present study, we report that simple photocapacitance spectroscopy can be used to detect the specific signature of positively charged trions of indirect excitons (IX^+) at moderate levels of carrier densities ($<1 \times 10^{11} \text{ cm}^{-2}$) as well as Fermi edge singularities (FESs) in higher level of carrier densities ($>1 \times 10^{11} \text{ cm}^{-2}$) in a single barrier GaAs/AlAs p-i-n heterostructure. We had already demonstrated [18] that photocapacitance spectroscopy can be used as a sensitive electro-optical tool to probe spatially indirect excitons formed across the AlAs potential barrier in GaAs/AlAs/GaAs heterostructure even at room temperature. The work described in this manuscript is a direct continuation of that recent work [18]. Here, we argue why photocapacitance can sense these IX^+ s even at 100 K, which was not possible to detect with photoluminescence. Formations of triangular quantum wells (TQWs) around Γ -AlAs potential barrier also help these spatially indirect trions to survive even at such temperature. We establish that photocapacitance spectroscopy is a more sensitive experimental technique for detecting trions and many body effects like FES than PL in such heterostructures. We also demonstrate that it is possible to probe and monitor the dielectric properties of strongly correlated, interacting dipoles of excitons, trions and FES using such capacitance-based techniques even at 100 K. In fact, these dipolar properties of excitonic complexes were mostly neglected in standard optical emission based spectroscopic techniques used in past studies to probe excitonic Bose-Einstein condensation (BEC) and excitonic lasing etc.

II. SAMPLE AND EXPERIMENTAL METHODS

The heterostructure used in this work was grown by molecular beam epitaxy on a semi-insulating GaAs (311)A substrate. A highly doped 1.5 μm buffer layer of p-GaAs ($4 \times 10^{18} \text{ cm}^{-3}$) was first grown on the substrate. This layer was used as the bottom electrical contact for our measurements. This was followed by a 100 nm thick p-GaAs ($1 \times 10^{17} \text{ cm}^{-3}$) layer. Then an 8 nm thick, undoped AlAs potential barrier having 100 nm thick undoped GaAs spacer layers on both sides were grown. Finally, a 100 nm n-GaAs ($2 \times 10^{16} \text{ cm}^{-3}$) layer and a 0.5 μm highly n-doped GaAs ($4 \times 10^{18} \text{ cm}^{-3}$) capping layer were grown to complete this heterostructure. Arrays of circular ring shaped gold mesas with diameter 400 μm and area of $\sim 5 \times 10^{-4} \text{ cm}^2$ were fabricated as top metal contacts. These mesas also facilitated optical access from the top of the device.

We used Agilent's E4980A LCR meter with 30 mV of rms voltage at 200 Hz frequency (unless mentioned otherwise) for phot capacitance measurements. Photocapacitance ($C_{\text{Photo}} = dQ/dV$) was measured under applied reverse bias while our sample was illuminated from the top n-GaAs side. Photocurrent measurements were performed using the same LCR meter in the DC mode as well as with Keithley 2611 source meter. An Acton Research's SP2555 monochromator having 0.5 m focal length (with $\Delta\lambda \sim 1.5 \text{ nm}$) along with 1000 Watts quartz-tungsten-halogen lamp was used for phot capacitance spectroscopy. Spectral response of lamp, monochromator combination was reasonably smooth and changes slowly and monotonically within the wavelength ranges used in our experiments. PL spectra were measured using a 35 mW He-Ne gas laser and CCS200 compact spectrometer from Thorlabs with spectral accuracy $< 2 \text{ nm}$ FWHM @633 nm. For temperature variation, we used a closed cycle Helium gas CS-204S-DMX-20 cryostat from Advance Research Systems along with the Lakeshore (Model-340)

temperature controller. A schematic diagram of GaAs/AlAs single barrier p-i-n heterostructure and the experimental set up of phot capacitance measurement are shown in Fig. 1(a).

Photocapacitance spectra at 100 K were measured under an optical intensity of $17.4 \mu\text{W}/\text{cm}^2$ at peak wavelength of 830 nm under reverse bias. In this work, we will only focus on the sharp resonant peak like spectral features in photocapacitance under non-zero biases. We carefully selected top mesa contacts for which DC-photocurrents are restricted within nano-Ampere ranges under reasonably small applied biases of a few volts. This prevents unwarranted dielectric screening of Coulomb attractions required to form these excitonic complexes. The applied electric fields corresponding to each bias have been estimated by dividing the bias magnitude with the thickness (~ 208 nm) of the intrinsic region of the heterostructure.

Previously, indirect excitons were usually created and probed using external gate voltages to tear apart direct excitons formed inside a single quantum well or in coupled quantum wells. However, these procedures often broaden the excitonic spectra and thereby compromise the nature of these excitons. On the other hand, here the applied electric fields are mainly utilized to push electrons and holes towards each other to form spatially separated, indirect excitons, trions, FES across the Γ -AlAs potential barrier. We had already shown [18] that this actually results in uncharacteristic sharpening of photocapacitance spectral features of indirect excitons with increasing bias. For more detailed comparisons, readers are can see Ref. [18].

III. RESULTS AND DISCUSSIONS

A. Bias dependent splitting in photocapacitance spectra leads to positively charged trions and Fermi edge singularity at 100 K

In the present article, we investigated bias induced formation dynamics of spatially indirect excitons and trions near the GaAs/AlAs/GaAs heterojunction under light and also under applied reverse biases around 100 K. In Fig. 1(b), changes in photocapacitance spectra under different applied reverse biases are shown. As the magnitude of reverse bias increases from -0.1 V to higher values, single resonant peak like excitonic spectra is split up into two distinctly separate peaks. This kind of peak splitting with increasing bias was clearly absent at room temperature [18]. Initially the spectral shapes of these peaks remain nearly symmetric until the bias value of -0.6 V. After this, an asymmetric spectral shape emerges where the low energy spectral tails rise slowly and the high energy side falls sharply. In addition, an enhancement of the low energy peak is clearly noticeable around -0.8 V and beyond. On the other hand, the higher energy peak almost vanishes gradually at larger biases.

To understand the above observations, a schematic band diagram of the GaAs/AlAs/GaAs heterojunction is drawn in Fig. 1(c) following previous reports [18,19,20]. We will not go into details of these X and Γ valley contributions on the carrier transport which was already well investigated and discussed earlier [18]. Under the above mentioned experimental conditions, we expect [18] the formation of hole accumulation layers in the form of 2D hole gas (2DHG) within the GaAs TQW near Γ -AlAs barrier in the top n-type GaAs layer above a certain bias. Similarly, we expect to have electron accumulation layer as 2D electron gas (2DEG) forming inside the TQW on the p-type GaAs side. These accumulated electrons and holes can form hydrogenic bound states of indirect excitons (IX^0) due to their mutual Coulomb attractions as reported earlier

[18]. This schematic diagram matches with the standard solution of self-consistent one dimensional Schrodinger and Poisson equations as described in earlier reports [21,22]. The 2DEG is spatially separated by 8 nm thin AlAs barrier from the 2DHG. The presence of this extra potential barrier in tunnel diode structure may introduce further complexities in such calculations. Additional charge accumulations in TQWs can lead to solutions of Poisson equation which are not [21] fully self-consistent with the Schrodinger equation for such resonant tunneling structures. Due to the dominant presence of Γ -AlAs potential barrier [18], the equilibrium charge transfer and band alignment of this heterojunction is significantly different from a normal p-i-n diode. We also expect the presence of both electrons and holes within respective TQWs inside this heterojunction. Therefore, we purposely avoided any quantitative estimation of carrier density using standard capacitance-voltage plot which is strictly based on depletion approximation and the presence of a single type of majority carriers.

However, we understand that large numbers of electrons and holes can accumulate in these TQWs to form 2DEG and 2DHG, respectively, with increasing reverse biases. As a result, corresponding carrier densities in each TQW also increase. So the charge density of photo generated carriers per unit area (σ_{ph}) around the heterojunction for each bias values can be estimated from Fig. 1(b) using the following relationship [8]

$$\sigma_{ph}e = CV \quad (1)$$

where e is the electric charge and C is the peak value of excitonic photocapitance per unit area at each applied bias (V). Following the description in Fig. 1(c), it is important to note here that one can also relate this σ_{ph} to the density of dipolar charges per unit area in a standard parallel plate capacitor configuration as

$$\sigma_{ph} = \vec{P} \cdot \hat{z} \quad (2)$$

where \vec{P} is the effective polarization of these excitonic dipoles around the AlAs barrier and \hat{z} is the unit vector along the growth direction.

At high enough injected carrier density, another peak at the low energy side starts to appear. This happens with $\sigma_{ph} > 3 \times 10^{10} \text{ cm}^{-2}$ or reverse biases greater than $|-0.3| \text{ V}$ as shown in Fig. 1(b). Evidently, concentrations of holes in the 2DHG become larger compared to those of electrons in 2DEG. This is because the sample is optically excited from the top n-GaAs side only and bias is also applied in the reverse direction. Such excess of one type of carriers (in our case holes) favor the formation of positively charged trions which can be controlled by both light or bias [23]. As a result of this excess hole density in 2DHG, we now ascribe the sharp resonant spectral features on the low energy side of the spectra with positively charged indirect excitons or trions (IX^+). Until the bias value reaches -0.6 V or $\sigma_{ph} \sim 8 \times 10^{10} \text{ cm}^{-2}$, both peaks look nearly symmetric. Even though, we see that the trion peak is getting bigger than the exciton peak. This low energy IX^+ state is more energetically favorable and tends to dominate at even higher applied biases.

Subsequently, after the reverse bias around -0.8 V , we observe another drastic change in the spectral behavior as evident from Fig. 1(b). The low energy trion peak indeed rises significantly whereas the exciton peak almost vanishes around $\sigma_{ph} \sim 1.2 \times 10^{11} \text{ cm}^{-2}$. Moreover, the spectral shape of this trion peak gradually becomes asymmetric in nature. This type of spectral transition is usually [15-17,24] identified with Fermi edge singularities at high enough carrier densities. Correspondingly, in our photocapacitance spectra, we see similar sharp, asymmetric enhancement of the trion peak once the photo generated density approaches $\sigma_{ph} \sim 1 \times 10^{11} \text{ cm}^{-2}$. In the present case, it is likely that at high photo generated carrier densities, localized hole states of

2DHG or holes in shallow impurity states can experience enhanced Coulomb attraction with the Fermi sea of electrons in 2DEG at such low temperatures. As a result, we observe a significant enhancement of optical absorption of this trion related FES. Previously, Yusa et al. [15] had reported asymmetric line shape in the absorption spectra which showed fast rise in the low energy side and slow fall in the high energy side. Chen et al.[16] and Skolnick et al. [17] had observed slow rise in the low energy side and fast fall in the high energy side of the PL spectra. Usually in the high density limit, enhanced carrier-carrier scattering broadens the high energy tail of FES. However, we notice that phot capacitance spectra in Fig. 1(b) have much sharper high energy edge in a system consisting of both 2DEG and 2DHG. In addition, we still see the remnant excitonic state above the FES. At the end of this section, we will again discuss how sub-band gap localized states may significantly modify the phot capacitance spectral broadening in the lower energy side of FES.

Nevertheless, in the common understanding of FES inside a quantum well structure, usually a sea of electrons in the conduction band is attracted to a single localized hole state near the valence band. This usually shows a power law singularity [15] of the form

$$A(\omega) = \frac{1}{|\omega - \omega_0|^\alpha} \quad (3)$$

in the absorption spectra where ω is the angular frequency of incident light, ω_0 is the resonant angular frequency of the absorption peak and α is a power law exponent. At -0.8 V, we found $\alpha \approx 0.4$, albeit from the low energy tail of the FES spectra. This value, however, matches with the literature [15]. At this stage, it is important to reiterate that here we are actually dealing with the dual presence of both 2DEG and 2DHG. In a way, we are looking at how a Fermi sea of

electrons inside a 2DEG interacts with excess holes localized around 2DHG. We will explain this in more detail at the end of this section.

We also note that the full widths at half maxima (FWHM ~ 8 meV) of these FES peaks are somewhat lower than the corresponding thermal width $\sim k_B T = 8.7$ meV at 100 K. So we can assume that this FWHM may provide an estimate of the Fermi Energy following the discussion by Skolnick et al. [17]. The 2D Fermi energy is usually calculated using the expression of (for spin $\frac{1}{2}$ particles)

$$E_F = \frac{\pi \hbar^2 \sigma_{ph}}{m^*} \quad (4)$$

where \hbar is the reduced Planck's constant, σ_{ph} is the dipolar charge density per cm^2 . Here, for these excitonic dipoles around the AlAs barrier, we have used $m^* = \mu$ as the reduced mass of holes and electrons $\sim 0.056 m_0$ in GaAs, m_0 is the free electron mass. Therefore, using Eq. (4), we find that $\text{FWHM} \sim E_F = 8 \text{ meV}$ corresponds to $\sigma_{ph} \sim 1.86 \times 10^{11} \text{ cm}^{-2}$ (following the discussion of Skolnick et al. in Ref. [17]). This estimate matches closely with $\sim 1.82 \times 10^{11} \text{ cm}^{-2}$, deduced from Eq. (1) at a bias of -1.0 V around where the prominent signatures of FES like asymmetric spectra is visible.

In TQWs, we understand that only the first few states of these 2DEG or 2DHG can remain strongly quantum confined, i.e. behave as two dimensional in nature. Higher energy states in TQWs are less localized as the well width becomes wider [21]. We understand this from the quantized energy E_n and n th eigenfunctions $\psi_n(z)$ of an infinite barrier TQW [22], which are given by

$$E_n \sim \sqrt[3]{\left[\left(\frac{\hbar^2}{2m^*} \right) \left[\frac{3\pi e F_z}{2} \left(n - \frac{1}{4} \right) \right]^2 \right]} \quad (5)$$

and

$$\psi_n(z) = Ai \left[\frac{2m^* eF_z}{\hbar^2} \left(z - \frac{E_n}{eF_z} \right) \right] \quad (6)$$

where $n = 1, 2, 3, \dots$, $Ai(z)$ is the Airy functions, m^* is the effective mass of electron/hole, e is the electronic charge, F_z is the electric field along the growth direction along z axis, \hbar is the reduced Planck's constant. The ratio of the first excited energy to the ground state energy is $\frac{E_2}{E_1} = \sqrt[2/3]{\left(\frac{7}{3}\right)} \sim 1.76$. Therefore, it is expected that in practice, with a finite barrier TQW like those shown in Fig. 1(c), only the ground state energy may remain strongly bound and quantum confined. However, with increasing bias and charge accumulations around the AIAs barrier, the quasi Fermi levels can suddenly penetrate these TQWs at the onset of FES. As a result, we also observe a sharp transition around a reverse bias of -0.8 V where the exciton-trion spectra suddenly convert into asymmetric FES spectra. This is because, with increasing bias, the quasi Fermi level E_{Fn} (E_{Fp}) of electrons (holes) can get pinned with the discrete ground state energy of 2DEG (2DHG) in these TQWs. However, the quasi Fermi Level separation ($E_{Fn} - E_{Fp}$) can vary along with the ground state energy levels of these electron and hole TQWs as shown in Fig. 1(d). As a result, we find that ($E_{Fn} - E_{Fp}$) can keep on increasing with the increase of reverse bias (electric field) as per Eq. (5). In the absence of any quantum confined excited states in these shallow TQWs, the maximum optical absorption energy for indirect excitons can then be limited by

$$E_{Opt}^{Max} = E_g + E_1^e + E_1^{hh} \equiv (E_{Fn} - E_{Fp}) \quad (7)$$

where E_g is the bulk bandgap of GaAs, $E_1^e(E_1^{hh})$ is ground state energy of electrons (heavy holes). In fact, we observe FES related enhancement at this E_{Opt}^{Max} edge only. In Fig. 1(d), we pictorially depict both high and low energy portion of this FES transition as $E_{high}(=E_{Opt}^{Max})$ and E_{low} following our schematic diagram given in Fig. 1(c). We assume that quantum confined holes in 2DHG can be further localized to shallow impurity states or interface trap states or to states related to alloy disorder inside 2DHG near the valence band edge. Any optical absorption from such shallow states near the 2DHG to E_1^e can couple the holes left in these localized states with the 2DEG to create the FES. So Fig. 1(d) can also explain the broad low energy tail (E_{low}) of the FES spectra as compared to its much sharper high energy side (E_{high}) as found in Fig. 1(b). Such relative sharpness of the high energy edge of FES can be traced back to intrinsic sharpness of respective Fermi edges as given in Eq. 7. All these understandings are schematically described in Fig. 1(d) and fully support our above explanations based on the formation of positively charged IX^+ at lower bias levels.

B. Red shift and binding energy of indirect trions at 100 K

To picture the above explanations, in Fig. 2(a), we use a 2D color filled contour plot of Fig. 1(b). This graphic presentation is essential for better visibility of spectral splitting, red shift of low energy IX^+ peak and energy separation of both exciton and trion peaks. Eventually the low energy trion peak leads to FES with increasing reverse biases. The dashed lines are drawn to guide the eyes only. A clear red shift of IX^+ spectra with the applied bias is visible as mentioned above, whereas there is hardly any shift in peak energy for IX^0 line. At this stage, it is not clear why excitonic peak at slightly higher energy is not at all affected by increasing the electric field.

Besides, applied voltage dependent spectral energy separation between two peaks clearly changes and increases with increasing bias as evidenced from the two dashed lines drawn in Fig. 2(a).

Following Bugajski and Reginski [25], we now discuss the transformation of trions into FES spectra. In the parabolic band approximation, the Fermi energy E_{Fn} of electrons in the bulk can be written in the form of low energy onset of absorption (ϵ_F) and emission edge (ϵ_g) as

$$E_{Fn} = (\epsilon_F - \epsilon_g) \left(1 + \frac{m_e^*}{m_h^*}\right)^{-1} \quad (8)$$

where $\left(\frac{m_e^*}{m_h^*}\right)$ is the effective mass ratio of electron and hole of GaAs. The Fermi energy varies with photo generated carrier density. As discussed above, we are driving both photo generated electrons and holes towards the AlAs barrier. So, the gap between the quasi Fermi levels ($E_{Fn} - E_{Fp}$) should increase with increasing bias. However, this change in E_{Fn} can be more in comparison to changes in E_{Fp} , because, in general, Fermi levels are inversely proportional to effective mass of the respective carrier and $\left(\frac{m_e^*}{m_h^*}\right) \ll 1$. As there is no observed change in the low energy onset ϵ_g of photoluminescence (as will be shown later) with increasing reverse bias, we may infer that ϵ_F may actually blue shift with increasing bias. Here we assume that any change in the effective mass ratio as a result of bias induced changes in the shape and size of TQWs is negligible. Consequently, FES related enhancement of photocapacitance spectra at $E_{Opt}^{Max} = (E_{Fn} - E_{Fp})$ should also show blue shift with increasing reverse bias greater than -0.8 V. However, we see the opposite effect and the high energy edge of FES actually red shifts. As mentioned above, in this case FES is a many body excitonic effect involving both 2DEG and

2DHG. Therefore, understanding the red shift of FES peak will not be possible without considering how these indirect excitonic complexes and Fermi levels are evolving with increasing bias in such heterostructure. From our recent report [18] on room temperature indirect excitons, we understand that the electrons and holes of IX^+ can come closer with increasing bias. Consequently, the binding energy of this IX^+ can increase with increasing bias. This can lead to the observed red shift of this trion FES edge due to opening up of an excitonic gap. On the other hand, this significant ~ 10 meV red shift of IX^+ line with the applied bias in this coupled TQWs structure may also be related to quantum confined Stark effect (QCSE) where exciton peaks usually broaden with increasing electric field.

The magnitude of this peak splitting initially increases slowly and then in the higher bias regime it varies significantly as also reported by Yusa et.al. [15]. With increasing bias the carrier density also increases which eventually contributes to strong scattering mechanisms [21]. However, rigorous explanation of spectral broadening of FES requires understanding the full picture of many body scattering mechanisms and extrinsic carrier dynamics within such single barrier heterostructure, which is currently beyond the scope of this study. However, in Fig. 2(b), spectral red shift of the trion peak energy has been fitted with linear dipole moment equation

$$E = E_0 + \vec{p} \cdot \vec{F} \quad (9)$$

where E is peak energy of IX^+ , E_0 is the energy at zero applied field, \vec{p} is the effective permanent dipole moment of these trions and \vec{F} is the applied electric field. We can see that \vec{p} and \vec{F} are directed opposite [18] to each other (see Fig. 1(c)). In addition, \vec{p} is anticipated to be independent of \vec{F} at such low temperature because of the observed linear variation of E with \vec{F} (see Fig. 2(b)). Two regions of the bias dependent photocapacitance spectra have been fitted with

two separate straight lines with slopes m_1 and m_2 . These slopes actually estimate the values of respective dipole moments. Slope m_1 corresponds to the dipole moment value $\sim 2.96 \times 10^{-28}$ C-m before the onset of FES. However, we get substantially larger value of this dipole moment from slope $m_2 \sim 7.97 \times 10^{-28}$ C-m for higher bias region when FES get started. In higher electric field regime, there will be more carrier injections to the TQWs. Following Eq. 2 and Fig. 1(d), this eventually contributes to larger dipolar polarizations as compared to that in lower biases.

As can be seen in Fig. 2(c), the peak intensity ratio of the peaks IX^+ and IX^0 varies slowly at the beginning. It then changes significantly with increasing applied electric fields. The ratio remains near unity in the low bias side, indicating equal contribution from both excitons and trions. However, with increasing biases, the trions start to dominate the photocapacitance spectra. This is because positive trions formation is always more energetically favorable compared to the excitons. As a result, the peak photocapacitance ratio of trions and excitons is shown to vary with the applied field, implying the formation of trions at the expense of excitons with the increase of electric field in the reverse bias regime. We tried to fit the above variation with a modified Arrhenius rate (R^*) equation following our earlier work [26]

$$R^* \approx \frac{1}{\tau} = \nu^* \exp\left(-\frac{E_a}{k_B} \eta V_{dc}\right) \quad (10)$$

where η is a proportionality factor in units of $V^{-1}K^{-1}$ to ensure correct dimensionality and E_a is activation energy for transitions activated by bias voltage V_{dc} , ν^* is the thermal pre-factor representing the heat bath, τ is the time period of the transition and k_B is the Boltzmann constant. The experimental data on peak photocapacitance ratio in Fig. 2(c) fits well with such bias activated model. The ratio drastically increases around the reverse bias of -0.8 V.

We have already mentioned that exciton peaks gradually decrease and hardly shift in energy with increasing applied bias, whereas the trion peaks slowly enhance and red shift drastically after certain applied bias. This can happen if more and more positively charged trions (IX^+) form at the expense of excitons (IX^0) in the presence of excess holes. Moreover, the trion peak ultimately converts to FES after a certain density regime which is in our case around $1 \times 10^{11} \text{ cm}^{-2}$. This understanding matches well with explanations provided by Huard et al. [27]. Accordingly, we plot the energy difference between two peaks with the estimated Fermi energy for each applied bias in Fig. 3. This is then linearly fitted with the following relation [8,27].

$$E_{IX^0} - E_{IX^+} = E_{IX^+}^b + E_{Fp} \quad (11)$$

Where $E_{IX^+}^b$ is the positive trion binding energy, E_{IX^0} and E_{IX^+} are peak energies for indirect excitons and positive trions respectively and E_{Fp} is the Fermi energy change due to extra holes in the valence band. E_{Fp} is estimated from photo generated carrier density using Eqs. (4), (1) with effective mass of hole as $m_h^* \sim 0.45 m_0$ in GaAs. From the intercept, we estimate the value of an average trion binding energy of $E_{IX^+}^b \sim 2.0 \text{ meV}$. However, we are also assuming here that the estimated value of $E_{IX^+}^b$ using the above Eq. (11) is independent of applied bias. Interestingly, it matches well with earlier reported value in GaAs/AlAs system [5-7,11]. This supports our spectroscopic confirmation of the presence of trions (IX^+) using photocapacitance. Whereas, previous reports mostly estimate this binding energy from PL measurements, here we show that trion binding energy can also be determined from photocapacitance spectroscopy.

Moreover we note that dissociation of either excitons or trions inside a solid is always a many body statistical process with thermodynamic dissociation probability $\sim \exp\left(-\frac{E^b}{k_B T}\right)$,

where E^b can be either the exciton or the trion binding energy [23,28,29]. This is because, such dissociations are typically governed by the following Saha's ionization equations [28,29].

$$\frac{n_h n_e}{n_{X^0}} = \frac{C_{X^0}^2}{C_e^2 C_h^2} \exp\left(-\frac{E^b_{X^0}}{k_B T}\right) \quad (12)$$

$$\frac{n_X n_h}{n_{X^+}} = \frac{4C_{X^+}^2}{C_X^2 C_h^2} \exp\left(-\frac{E^b_{X^+}}{k_B T}\right) \quad (13)$$

where $E^b_{X^0}$, $E^b_{X^+}$ are binding energies of excitons and positively charged trions, n_i are carrier densities per unit area, $C_i = \hbar \sqrt{\frac{2\pi}{m_i k_B T}}$ are thermal wavelengths and m_i are effective masses of ($i = e, h, X^0, X^+$) electrons, holes, excitons and trions respectively as in Ref. [28].

Most importantly, assuming constant pre-factors to the exponential term in equations 12 and 13, we note that $\exp(-2) \approx 0.135$, $\exp(-1) \approx 0.368$, $\exp(-0.5) \approx 0.607$ when the all-important ratio $\left(\frac{E^b_i}{k_B T}\right)$ varies from 2 to 1 to 0.5, respectively. This clearly shows that even when the binding energy E^b_i is less than the thermal fluctuation energy ($k_B T$), there still can be a finite, *non-zero* probability of having some bound states of excitons or trions. It is remarkable to discover that photocapacitance spectroscopy is still sensitive to these very small numbers of excitons or trions. As such, we already know [18] that binding energies can also change under applied bias and can also thereby affect the above populations. However, such changes can be quite small (see Fig. 5(b) of Ref. [18]). Therefore, based on the above numerical estimates, unless the ratio $\left(\frac{E^b_i}{k_B T}\right)$ varies hugely, it need not affect the final population significantly.

C. Differences in spectra at a fixed bias and with respect to temperature

Photocapacitance and photo- G/ω spectra at 200 Hz are compared with DC-photocurrent spectra for -0.6 V bias at 100 K as shown in Fig. 4(a). Spectral splitting is only observed in photocapacitance spectra whereas we don't see any spectral splitting in photocurrent and photo- G/ω . Also there is a slight shift in peak energy position observed among these. Such differences were also observed at room temperature and were attributed [18] to dissociation of direct excitons which are not closer to the AIAs potential barrier. We would like to mention here that a simple equivalent circuit consisting of capacitance (C) and conductance (G) in parallel was used to extract photocapacitance using LCR meter such that $|C|$ is always greater than $|0.1 \times G/\omega|$ where $\omega=2\pi f$. We know [18] that photocapacitance arises mainly from the bias driven accumulated charge carriers near the AIAs barrier whereas the DC-photocurrent is solely affected by the charge carriers driven out of the junction. However, contributions to photo- G/ω can come from both these regions. Moreover, one can notice that the spectral broadening in the photocurrent spectra is reasonably higher than the photo- G/ω and photocapacitance at -0.6 V. All these certainly imply that the origin of DC-photocurrent spectra is different. Measured photocurrent is likely to originate from the dissociation of excitonic [30] photo absorptions, which are mostly forming away from the junction [18]. This will be further elaborated in Sec. III D.

In Fig. 4(b), we now explain how the temperature variation changes the photocapacitance spectral shape and the peak energy for this particular applied bias of -0.6 V. Here, we observe that the single excitonic peak at room temperature drastically changes to narrower double peaks of both excitons and trions at 100 K. This clearly indicates that such peak splitting occurs only at low temperature and also under high applied biases. Such a critical role of applied biases will

again be emphasized in the next Sec. III D. Blue shift of the spectral peak energies with decreasing temperature can be explained from the usual band gap expansion.

D. Advantages of photocapacitance spectra in comparison to PL spectra in studying such indirect excitonic complexes.

In most studies, PL spectra were mainly used to understand the intricate details of many body carrier dynamics of trions and FES. In Fig. 5(a) we plot the PL spectra at 100 K for different applied biases. The spectral broadening, i.e. full width at half maxima (FWHM), is certainly more than that of usual intrinsic FWHM of any excitonic PL at low temperature. However, unlike photocapacitance spectra, we do not observe spectral splitting and any spectral shift in the PL spectra under increasing reverse biases. Also this PL spectral peak energy is expectedly at a lower energy in comparison to the photocapacitance spectral peak. This definitely indicates two different physical origins for PL and photocapacitance spectra. Integrated PL intensity versus optical excitation intensity also follows a linear variation in log-log scale which gives a slope of ~ 0.96 at 100 K indicating [26] the presence of excitons as shown in Fig. 5(b). PL spectra are mostly unaffected by applied bias. PL is also a two-step probabilistic process involving photoexcitation and radiative recombination. It is expected that neutral, indirect excitons (IX^0 s) and positively charged, indirect trions (IX^+ s) around the AIAs barrier hardly contribute to PL due to the lack of spatial overlap of their respective electron and hole wave functions. Therefore, the observed PL is mainly due to the presence of excitons which are photo excited far away from the AIAs junction and then radiatively recombine. As a result, PL spectra are hardly affected by the applied bias. However, the indirect excitons, trions (IX^+), FES forming

near the heterojunction are strongly affected by the applied bias as shown in Figs. 1(c) and 1(d). As a result, such bias induced changes in carrier accumulations around the GaAs/AlAs/GaAs heterojunction can be sensed by photocapacitance.

As such absorption and emission spectroscopies are based on two different mechanisms where carrier dynamics and detection techniques are different. In fact, this difference is the exact reason why PL was not able to respond to applied bias and could not probe the all-important indirect excitons at such high temperature of 100 K even with more intense photoexcitation. This is because electron-hole pairs generated throughout the top GaAs also contribute significantly to PL. On the other hand, the radiative recombinations from spatially indirect excitonic many body systems are negligible. As reported previously [18] for indirect excitons, the photocapacitance spectroscopy is now shown to be also sensitive to bias induced dipolar changes of indirect trions, FES formed across the AlAs barrier. It is this enhanced selectivity of photocapacitance spectroscopy to these spatially indirect dipoles of excitonic many body systems like trions and FES which needed to be emphasized here. In the present article, we wanted to emphasize that photocapacitance spectroscopy is a superior technique in detecting these delicate indirect excitons, trions and FES in comparison with conventional PL spectroscopy.

In addition, we want to state that optical intensity dependence of photocapacitance spectra is also studied for fixed biases at 100 K (spectra are not shown here). Spectral peak splitting and shapes are observed to be hardly affected by the variation of the optical excitation intensity over the range 2 to 50 $\mu\text{W}/\text{cm}^2$. Increase of the optical excitation intensity only increases the magnitude of the overall photocapacitance. Interestingly, it is the applied bias which plays a more crucial role to inject the optically generated carriers to respective TQWs to form excitonic complexes. Therefore, we now have experimental proof that formations of these

spatially indirect trions and FES in this GaAs/AlAs/GaAs heterostructure can be predominantly controlled by the applied reverse bias and not so much by the optical excitation intensity.

IV. CONCLUSIONS.

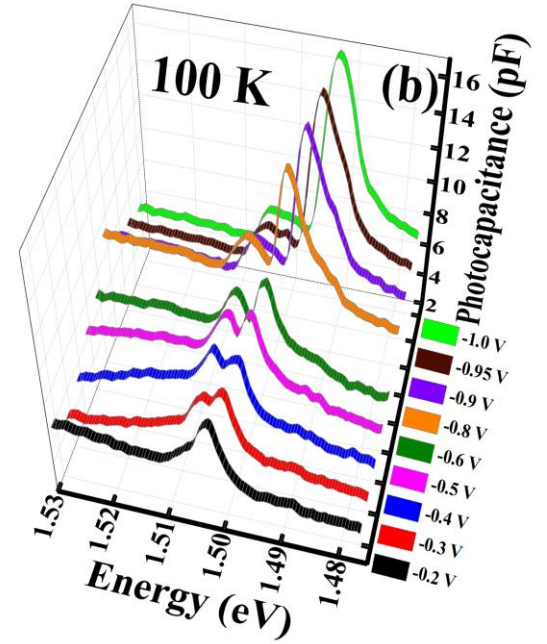
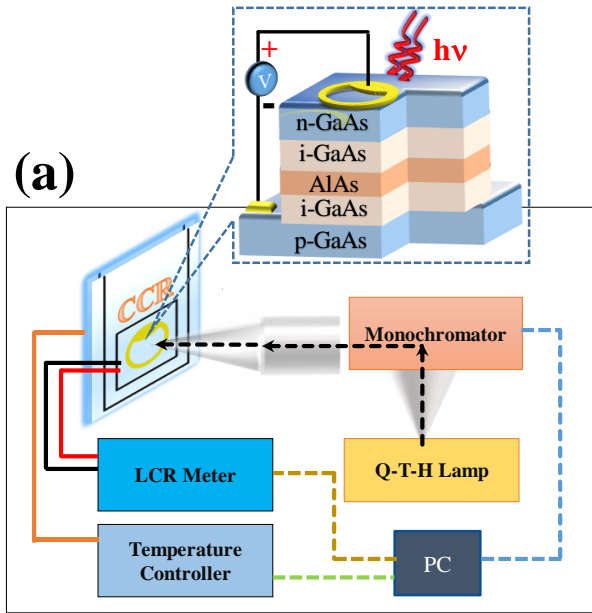
In summary, phot capacitance spectroscopy was used to detect the formation of spatially indirect, bias driven, dipoles of excitons as well as positively charged trions around the AlAs barrier in GaAs/AlAs/GaAs p-i-n heterostructure even at 100 K. Bias dependent spectral peak splitting of exciton and trions is also demonstrated. Moreover, in the higher density limit $\geq 1 \times 10^{11} \text{ cm}^{-2}$, we have also identified the signatures of Fermi edge singularity from phot capacitance spectra. Contrary to popular beliefs, the presence of trions at such a high temperature of $\sim 100 \text{ K}$ in these III-V materials is explained using the Saha's ionization equation. This analysis indicates that there is always a small but finite thermodynamic probability of existence of excitonic complexes having binding energy lower than the thermal bath energy ($k_B T$). Interestingly, we have shown that these small fractions of trions and excitons do respond to phot capacitance spectroscopy but not to conventional optical measurements like PL and DC-photocurrent spectra. Researchers mostly use PL to study these excitons, trions and FES in a variety of materials. However, it is established here that phot capacitance is a superior and sensitive experimental tool to probe and study these types of spatially indirect, many-body excitonic complexes in such single barrier p-i-n heterostructures. Our work also explains why and how phot capacitance spectroscopy can probe these interacting dipoles of trions and FES, which an ordinary luminescence spectroscopy fails to do so.

Such electrical detection and manipulation of excitons and trions at such high temperatures of 100 K was clearly unheard of in III-V materials. We predict that these observations provide a first concrete step towards any device level experimental control of trions and FES at even higher temperatures. This can further lead to future applications [3,31-33] in next generation optoelectronics and telecommunications devices, possibly even at room temperature, using similar heterostructures made with 2D monolayers of TMDC having high excitonic binding energies. Moreover, it is difficult to directly probe the ‘dark’ excitons’ with standard optical emission based spectroscopies. However, these kind of capacitive techniques [18,26], have the potential to even sense dipolar signatures of ‘dark’ excitons which constitute the true ground state of any excitonic BEC. Such indirect excitons in TMDC heterostructure are also predicted [34,35] to display excitonic superconductivity, electro-optical spectral control of trion lasing [36] and optical modulation [37] of ‘dipolar’ excitons. Therefore, our present and past [18,26] studies on frequency dependent dynamic signatures of dipolar nature of excitons and trions can provide significant impetus to explore simple photocapacitive spectral control of excitons, trions and FES for future applications.

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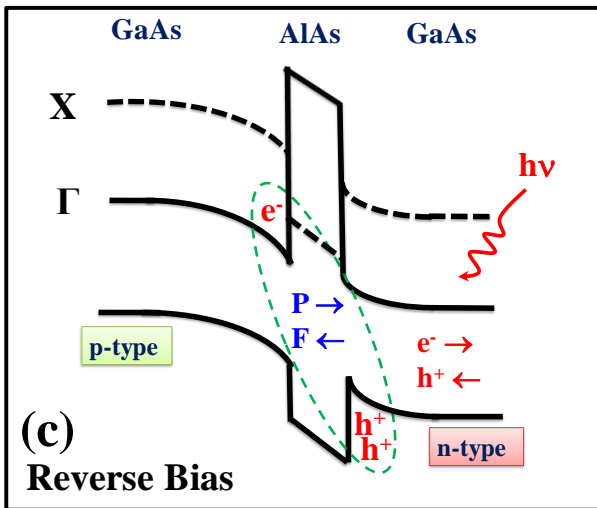
Authors acknowledge Department of Science and Technology, India (Research Grants # SR/S2/CMP-72/2012 and SR/NM/TP13/2016). We are grateful to Prof. B. M. Arora from IIT-Mumbai for his advice on band diagrams. AB and MKS are thankful to DST, India for Inspire PhD Fellowship and IISER-Pune for Integrated PhD Fellowship, respectively. YGG acknowledges the financial support from the Brazilian agency Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP) (Research Grants # 16/10668-7 and 18/01808-5). MH acknowledges support from the UK Engineering and Physical Sciences Research Council.

(a)



(c)

Reverse Bias



(d)

Reverse Bias

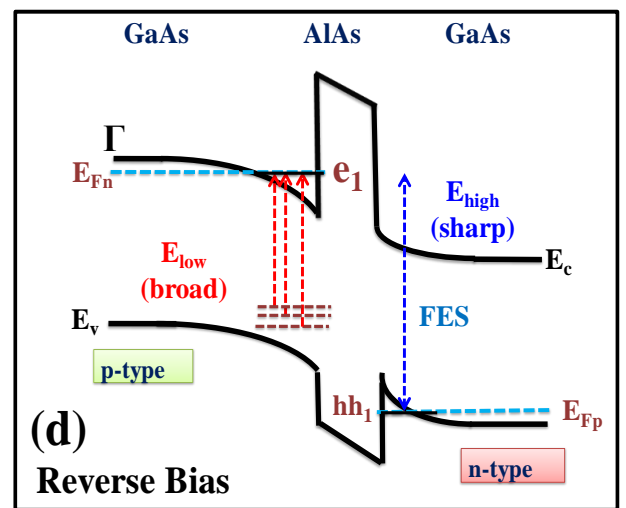


FIG. 1. (a) Schematic diagram of the experimental set-up for photocapacitance measurements is given here. Inset shows the sample structure. (b) Variation of excitonic photocapacitance spectra with optical excitation energy for different reverse biases at 100 K. A single excitonic peak splits up into two distinct peaks of exciton and trion with increasing applied biases. Low energy trion peak evolves into FES like asymmetric spectra at higher biases. The last four spectra from -0.8 V to -1.0 V are vertically shifted by 2 pF for better visibility. (c) Schematic band diagram of the reverse biased sample under light illumination from the top n-GaAs side. This is used to explain the formation of positively charged trions. (d) Origin of low and high energy tails of the FES spectra is schematically explained using a similar diagram. Relevant transitions contributing to low and high energy optical absorption tails are depicted respectively with red and blue arrows, respectively.

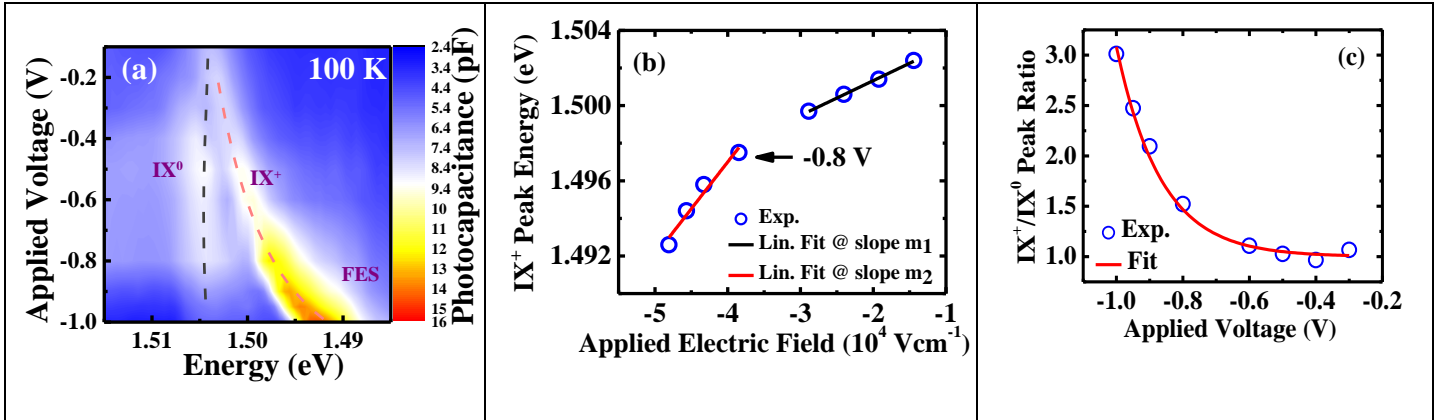


FIG. 2. (a) 2D colored contour plot of Fig. 1(b) is drawn. Two dashed lines are guiding to eyes only. Significant red shift of the IX^+ line and the visible splitting of the spectra with bias are clearly pointed out. In higher bias, the symmetric IX^+ line turns into Fermi edge singularity (FES) as the spectral shape become asymmetric. (b) Linear variation of peak energy of positively charged trion with increasing electric field is demonstrated to estimate the permanent dipole moments. There is a clear discontinuity around -0.8 V with a field of $-3.8 \times 10^4 \text{ V.cm}^{-1}$. This represents a distinct transition from trion like peak to FES like spectral signature. (c) Bias activated changes in the ratio of neutral exciton to positively charged trion components of the photocapacitance spectra is shown here.

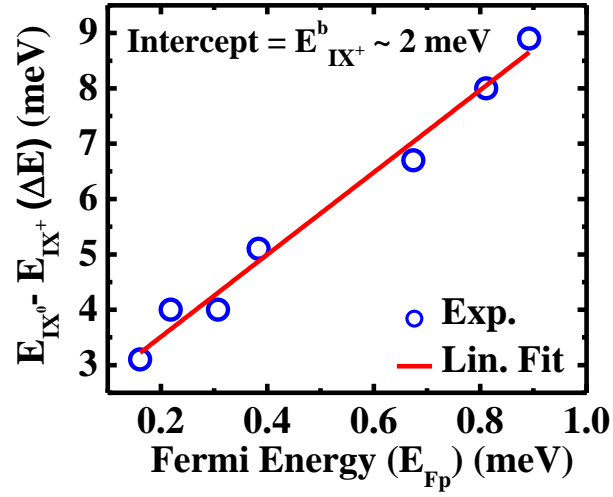


FIG. 3. Variation of peak splitting energy for excitons and trions with respect to the Fermi energy. The estimated trion binding energy matches well with past results in GaAs.

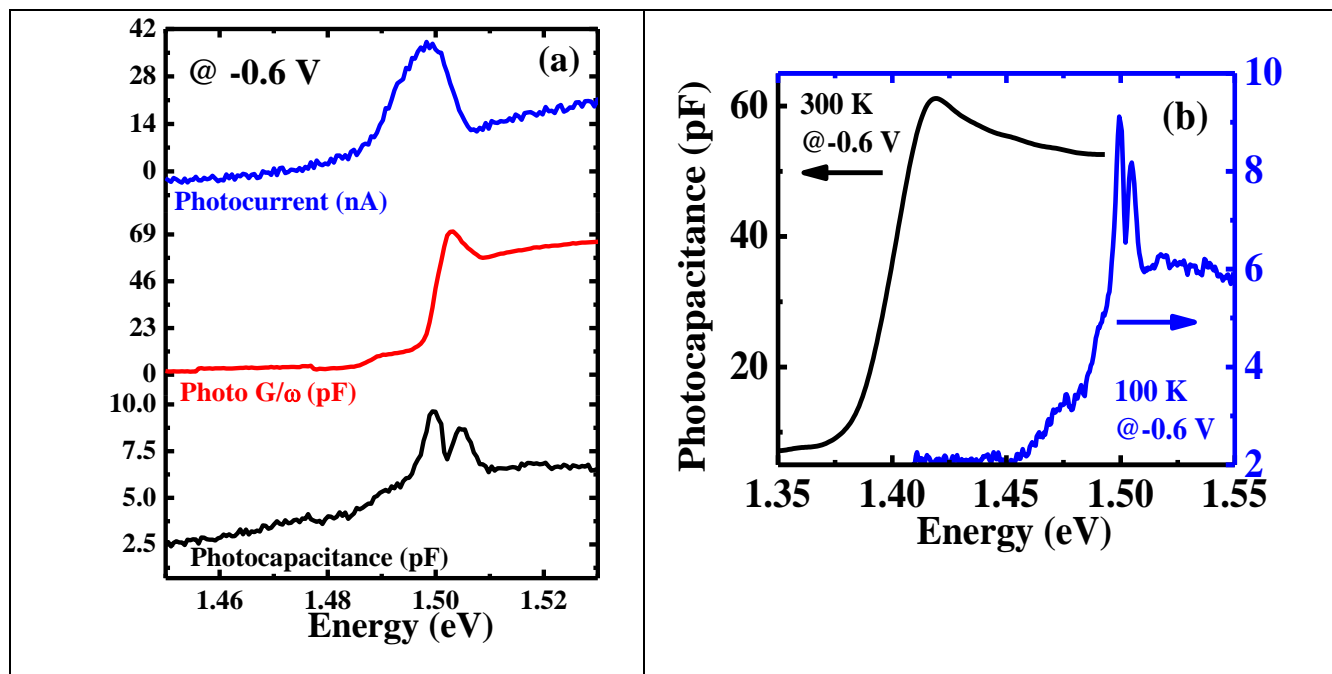


FIG. 4. (a) Photocapacitance and Photo- G/ω measured at 200 Hz is compared with DC-photocurrent Spectra for -0.6 V bias at 100 K. (b) Photocapacitance spectra at 100 K and 300 K are compared at a similar reverse bias of -0.6 V and frequency of 200 Hz. Spectral peak energy and spectral shape changed significantly with temperature.

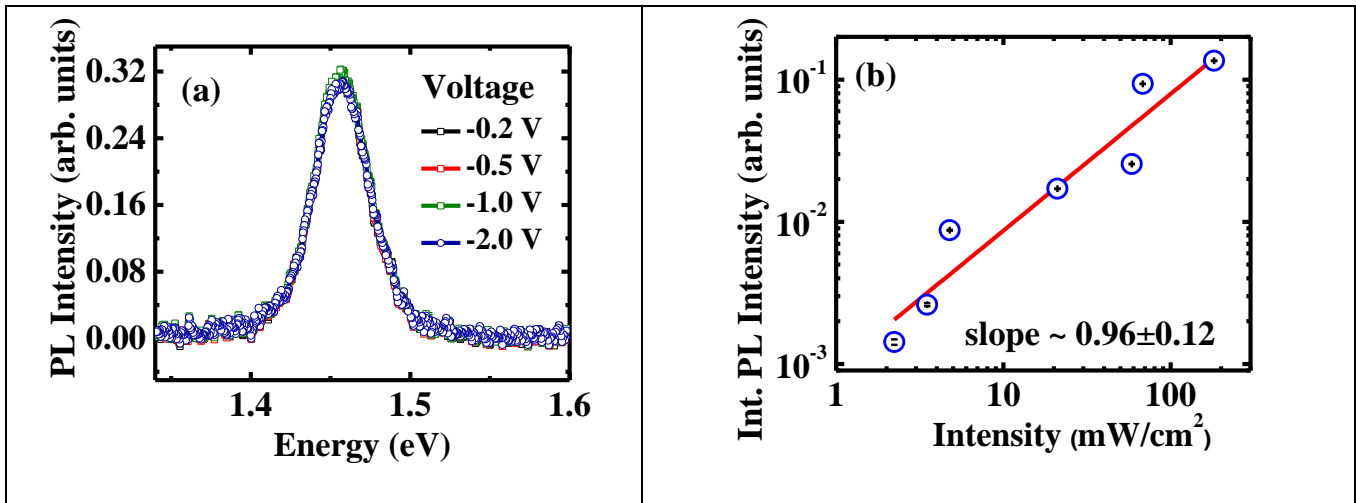


FIG. 5. (a) Photoluminescence Spectra at 100 K under different reverse biases. However, we did not observe any bias dependent spectral splitting and spectral red shift in the photoluminescence spectra. (b) Integrated PL intensity versus excitation intensity follows a linear variation in log-log plot which gives a slope ~ 0.96 at 100 K.

References:

- [1] B. Ganchev, N. Drummond, I. Aleiner, and V. Fal'ko, Three-particle complexes in two-dimensional semiconductors, *Phys. Rev. Lett.* **114**, 107401 (2015).
- [2] M. Zielinski, K. Golasa, M. R. Molas, M. Goryca, T. Kazimierczuk, T. Smolenski, A. Golnik, P. Kossacki, A. A. L. Nicolet, M. Potemski, Z. R. Wasilewski, A. Babinski, Excitonic complexes in natural InAs/GaAs quantum dots, *Phys. Rev. B* **91**, 085303 (2015).
- [3] L. V. Butov, Excitonic devices, *Superlattices Microstruct.* **108**, 2 (2017).
- [4] M. A. Lampert, Mobile and immobile effective-mass-particle complexes in nonmetallic solids, *Phys. Rev. Lett.* **1**, 450 (1958).
- [5] F. M. Peeters, C. Riva, and K. Varga, Trions in quantum wells, *Physica B: Condensed Matter* **300**, 139 (2001).
- [6] R. A. Sergeev, R. A. Suris, G. V. Astakhov, W. Ossau, and D. R. Yakovlev, Universal estimation of X^- trion binding energy in semiconductor quantum wells, *Eur. Phys. J. B* **47**, 541 (2005).
- [7] F. J. Teran, L. Eaves, L. Mansouri, H. Buhmann, D. K. Maude, M. Potemski, M. Henini, and G. Hill, Trion formation in narrow GaAs quantum well structures, *Phys. Rev. B* **71**, 161309 (2005).
- [8] K. F. Mak, K. He, C. Lee, G. H. Lee, J. Hone, T. F. Heinz, and J. Shan, Tightly bound trions in monolayer MoS₂, *Nat Mater* **12**, 207 (2013).
- [9] B. Zhu, H. Zeng, J. Dai, Z. Gong, and X. Cui, Anomalously robust valley polarization and valley coherence in bilayer WS₂, *Proc. Natl. Acad. Sci.* **111**, 11606 (2014).
- [10] B. Stébé and A. Ainane, Ground state energy and optical absorption of excitonic trions in two dimensional semiconductors, *Superlatt. Microstruct.* **5**, 545 (1989).
- [11] S. Glasberg, G. Finkelstein, H. Shtrikman, and I. Bar-Joseph, Comparative study of the negatively and positively charged excitons in GaAs quantum wells, *Phys. Rev. B* **59**, R10425 (1999).
- [12] G. D. Mahan, Excitons in degenerate semiconductors, *Phys. Rev.* **153**, 882 (1967).
- [13] P. Hawrylak, Optical properties of a two-dimensional electron gas: Evolution of spectra from excitons to Fermi-edge singularities, *Phys. Rev. B* **44**, 3821 (1991).
- [14] G. G. Spink, P. López Ríos, N. D. Drummond, and R. J. Needs, Trion formation in a two-dimensional hole-doped electron gas, *Phys. Rev. B* **94**, 041410 (2016).

- [15] G. Yusa, H. Shtrikman, and I. Bar-Joseph, Onset of exciton absorption in modulation-doped GaAs quantum wells, *Phys. Rev. B* **62**, 15390 (2000).
- [16] W. Chen, M. Fritze, A. V. Nurmikko, M. Hong, and L. L. Chang, Fermi-edge singularities and enhanced magnetoexcitons in the optical spectra of GaAs/(Ga,Al)As single quantum wells, *Phys. Rev. B* **43**, 14738 (1991).
- [17] M. S. Skolnick, J. M. Rorison, K. J. Nash, D. J. Mowbray, P. R. Tapster, S. J. Bass, and A. D. Pitt, Observation of a many-body edge singularity in quantum-well luminescence spectra, *Phys. Rev. Lett.* **58**, 2130 (1987).
- [18] A. Bhunia, M. K. Singh, Y. G. Gobato, M. Henini, and S. Datta, Experimental evidences of quantum confined 2D indirect excitons in single barrier GaAs/AlAs/GaAs heterostructure using photocapacitance at room temperature, *J. Appl. Phys.* **123**, 044305 (2018).
- [19] H. V. A. Galeti, H. B. de Carvalho, M. J. S. P. Brasil, Y. Galvão Gobato, V. Lopez-Richard, G. E. Marques, M. Henini, and G. Hill, Role of X valley on the dynamics of electron transport through a GaAs/AlAs double-barrier structure, *Phys. Rev. B* **78**, 165309 (2008).
- [20] J. J. Finley, R. J. Teissier, M. S. Skolnick, J. W. Cockburn, G. A. Roberts, R. Grey, G. Hill, M. A. Pate, and R. Planel, Role of the X minimum in transport through AlAs single-barrier structures, *Phys. Rev. B* **58**, 10619 (1998).
- [21] J. Singh, *Physics of Semiconductors and Their Heterostructures* (McGraw-Hill Inc., USA, 1992).
- [22] E. E. Vdovin, M. Ashdown, A. Patanè, L. Eaves, R. P. Campion, Y. N. Khanin, M. Henini, and O. Makarovskiy, Quantum oscillations in the photocurrent of GaAs/AlAs p-i-n diodes, *Phys. Rev. B* **89**, 205305 (2014).
- [23] A. Vercik, Y. G. Gobato, and M. J. S. P. Brasil, Thermal equilibrium governing the formation of negatively charged excitons in resonant tunneling diodes, *J. Appl. Phys.* **92**, 1888 (2002).
- [24] H. Kalt, K. Leo, R. Cingolani, and K. Ploog, Fermi-edge singularity in heavily doped GaAs multiple quantum wells, *Phys. Rev. B* **40**, 12017 (1989).
- [25] A. Bugajski and K. Reginski, Optical properties of semiconductor quantum wells, *Opto-Electr. Rev.* **4** (1996).

- [26] A. Bhunia, K. Bansal, M. Henini, M. S. Alshammari, and S. Datta, Negative activation energy and dielectric signatures of excitons and excitonic Mott transitions in quantum confined laser structures, *J. Appl. Phys.* **120**, 144304 (2016).
- [27] V. Huard, R. T. Cox, K. Saminadayar, A. Arnoult, and S. Tatarenko, Bound states in optical absorption of semiconductor quantum wells containing a two-dimensional electron gas, *Phys. Rev. Lett.* **84**, 187 (2000).
- [28] A. Esser, E. Runge, R. Zimmermann, and W. Langbein, Trions in GaAs quantum wells: Photoluminescence lineshape analysis, *phys. stat. solidi (a)* **178**, 489 (2000).
- [29] L. K. J. Szczytko, J. Berney, F. Morier-Genoud, M.T. Portella-Oberli, and B. Deveaud, Determination of the exciton formation in quantum wells from time-resolved interband luminescence, *Phys. Rev. Lett.* **93**, 137401 (2004).
- [30] M. Fox, *Optical properties of Solid* (Oxford University Press Inc., NY, 2010), 2nd edn.
- [31] V. Orsi Gordo, M. A. G. Balanta, Y. Galvão Gobato, F. S. Covre, H. V. A. Galeti, F. Iikawa, O. D. D. Couto, Jr., F. Qu, M. Henini, D. W. Hewak and C. C. Huang, Revealing the nature of low-temperature photoluminescence peaks by laser treatment in van der Waals epitaxially grown WS₂ monolayers, *Nanoscale*, **10**, 4807 (2018).
- [32] Wanshun Xia, Liping Dai, Peng Yu, Xin Tong, Wenping Song, Guojun Zhang and Zhiming Wang, Recent progress in van der waals heterojunctions, *Nanoscale* **9**, 4324 (2017).
- [33] A. Pospischil and T. Mueller, Optoelectronic devices based on atomically thin transition metal dichalcogenides, *Appl. Sci.* **6**, 78 (2016).
- [34] M. M. Fogler, L.V. Butov and K.S. Novoselov, High-temperature superfluidity with indirect excitons in van der Waals heterostructures, *Nature Communications*, **5**, 4555 (2014).
- [35] Oleg L. Berman and Roman Ya. Kezerashvili, High-temperature superfluidity of the two-component Bose gas in a transition metal dichalcogenide bilayer, *Phys. Rev. B* **93**, 245410 (2016).
- [36] J. Puls, G. V. Mikhailov, F. Henneberger, D. R. Yakovlev, A. Waag, and W. Faschinger, Laser action of trions in a semiconductor quantum well, *Phys. Rev. Lett.* **89**, 287402 (2002).

[37] S. Yu, X. Wu, Y. Wang, X. Guo, and L. Tong, 2D materials for optical modulation: challenges and opportunities, *Adv. Mater.* **29**, 1606128 (2017).