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Excitation energy dependence of the photoluminescence spectrum of an $In_xGa_{1-x}N/GaN$ single quantum well structure

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We have observed oscillations in the low temperature ($T < 50$ K) photoluminescence excitation spectra of an $In_xGa_{1-x}N/GaN$ single quantum well at photon energies above the GaN band gap. We attribute the features in the spectra to excitation of electrons at multiples of the LO phonon energy above the GaN conduction band edge. The rapid cooling of these electrons to the GaN conduction band edge and their subsequent capture leads to a shift, and hence the oscillations, in the photoluminescence spectrum. We interpret the shift in the spectrum as being due to a modification of the occupation of the distribution of localization centers.

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I. INTRODUCTION

Photoluminescence excitation (PLE) spectroscopy has proven[1,2] to be a particularly useful tool for the study of the optical properties of bulk and low dimensional semiconductor structures. In the main PLE has been used to measure the energies of the higher lying intersubband transitions in low dimensional systems. While it is true that a PLE spectrum is mainly determined by the form of the absorption spectrum, other physical processes can influence a PLE spectrum. This is because PLE spectroscopy involves energy relaxation of the photoexcited carriers to the emitting state being monitored. As an example, in the work of Weisbuch[1] strong oscillations were observed in the PLE spectra of bulk GaAs at a temperature of 1.7 K. When the intensity of the bound exciton photoluminescence (PL) was monitored the peaks of the oscillations occurred when the excitation photon energy E_n was

$$E_n = E_G + n\hbar\omega\left(1 + \frac{m_e}{m_h}\right), \tag{1}$$

where $n=1,2,3\ldots,\hbar\omega$ is the LO phonon energy, E_G the band gap, and m_e and m_h are the effective masses of electrons and holes in the conduction and valence bands, respectively. For these critical values of E_n a photoexcited electron can relax rapidly to the conduction band edge by the emission of one or more LO phonons. For photon energies not equal to E_n the electron relaxation can only occur by the slower process of emission of acoustic phonons. The overall consequence of this was that for E_n the effective electron temperature was reduced compared with other excitation photon energies. Whether the values of E_n coincided with maxima or minima in the PLE spectra depended on the consequences of the reduced electron temperature for the particular property being monitored.

Such LO phonon related features have been reported by others[3–5] where the effects appear due to different mechanisms depending on the system studied. Of particular relevance is the work reported by Ambrazevicius[5] who investigated the PLE spectra of InGaAs/GaAs single quantum well structures where the quantum well was situated different distances from the sample surface. For the sample where the quantum well was only 0.2 μm from the surface, strong oscillations were observed in the PLE spectra at energies whose maxima were described by Eq. (1). This effect was attributed to the combined effects of LO phonon assisted relaxation of electrons to $k=0$ and, because of the surface electric field, the fast transfer and subsequent capture of the nonthermalized electron distribution.

We must note one particular modification to this behavior; so far we have discussed only the excitation and LO phonon assisted scattering of free electrons to $k=0$, which is described by Eq. (1). As reported by others[6,7] peaks or dips can appear in PLE spectra that are not described by Eq. (1). These features have been attributed to cooling of hot excitons by the emission of LO phonon(s). The photon energies of these features are determined by precise nature of exciton/LO phonon interaction and will not be discussed in detail.

In this paper, we describe the results of PLE spectroscopy on a single InGaN/GaN quantum well. In particular we investigated the range of excitation photon energies above the GaN band gap where we saw features attributable to the creation of a nonthermal distribution of electrons. The reason for the appearance of these features will be discussed in the context of the particular sample studied and the nature of the PL spectrum.

II. EXPERIMENTAL DETAILS

The InGaN/GaN single quantum well structure was grown on a *c*-plane sapphire substrate by metal-organic vapor phase epitaxy in a 6 × 2 in. Thomas Swan Close Coupled Showerhead reactor. Trimethyl gallium (TMG), trimethyl indium (TMI), and ammonia (NH_3) were used as precursors and hydrogen and nitrogen as carrier gases. A GaN nucleation layer was grown at 540 °C, followed by a GaN epilayer with a nominal thickness of 4.5 μm grown at 1020 °C. The InGaN quantum well was grown at 770 °C with precursor flows of $F_{TMG}=4.6$ μmol/min and F_{TMI}

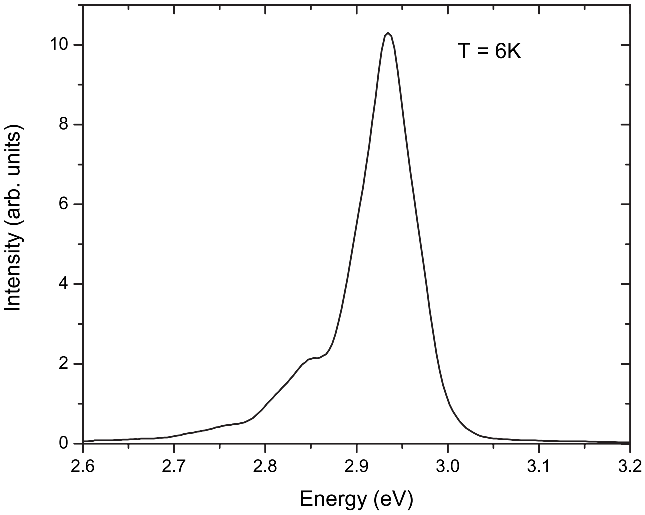

FIG. 1. Photoluminescence spectrum of InGaN/GaN quantum well measured at a temperature of 6 K with an excitation photon energy of 4.133 eV.

$=14.5$ μmol/min, while the GaN barrier was grown at 860 °C with a precursor flow of $F_{\mathrm{TMG}}=80.1$ μmol/min. The reactor pressure was held at 300 torr in a nitrogen atmosphere and an NH_3 flow of 446 mmol/min during the growth of the active region. A P'Analytical X'Pert MRD high-resolution x-ray diffraction instrument, using Cu $K\alpha$ radiation and a parabolic graded mirror, was used to analyze the sample. Using a combination of x-ray reflectivity and high-resolution x-ray diffraction[8] the $In_xGa_{1-x}N$ quantum well width, composition, and GaN capping layer thickness were determined to be 2.6 nm, $x=0.121$ and 10.3 nm, respectively. The optical studies were performed with the sample mounted on the cold finger of a closed cycle He cryostat. The sample was mounted at Brewster's angle and the emission was collected via a polarizer to remove the effects of multiple beam interference on the PL spectra.[9] The optical excitation was performed with chopped, tunable or fixed wavelength light from a high pressure Xe lamp dispersed by a 0.25 m spectrometer, the resolution of the spectrometer over the range of interest was ~10 meV. To remove errors involving the 0.25 m spectrometer the numerical values quoted for spectral features in the PLE spectra were obtained by measuring the wavelength of the scattered light using the double spectrometer. The PL from the sample was analyzed by a 0.85 m double grating spectrometer and detected by a cooled GaAs photomultiplier and standard lockin techniques. The excitation power density used for the spectra that are shown in this paper was 0.5 mW cm^{-2}.

III. RESULTS AND DISCUSSION

In Fig. 1 is shown the PL spectrum when the sample was at a temperature of 6 K and excited by light whose photon energy was 4.133 eV. The spectrum consists of a main feature with a peak energy of 2.935 eV which is attributed to the zero phonon recombination of localized electrons and holes as well as a series of peaks to lower energies due to LO phonon accompanied emission of the localized carriers.[9] PLE spectra were measured at various detection energies across the PL spectrum and the following general behavior observed as shown in Fig. 2. When detecting on the high energy side of the zero phonon emission line we observed PLE spectra similar to that shown in Fig. 2(a) whereas when detecting on the low energy side we observed PLE spectra similar to that shown in Fig. 2(b). The clear difference between the two types of spectra is that the series of **broad** and **sharp** *minima* (broad: 3.607, 3.710 eV, 3.802 eV, and 3.893 eV; sharp: $A=3.495$ eV and $B=3.530$ eV) in the PL intensity in Fig. 2(a) appear as a series of broad and sharp *maxima* in Fig. 2(b). To understand this behavior we measured the PL spectra (see Fig. 3) using excitation photon energies of 3.607 and 3.663 eV. These photon energies are as indicated in Fig. 2. As can be seen in Fig. 3 the effect of the different excitation photon energies is to shift the PL spectrum. Thus the reason why the oscillations in the PLE spectra shown in Fig. 2 are "180° out of phase" is that at the critical excitation photon energies the PL spectrum shifts causing a decrease (increase) in the PL intensity when the PL intensity is monitored on the low (high) energy side of the PL spectrum.

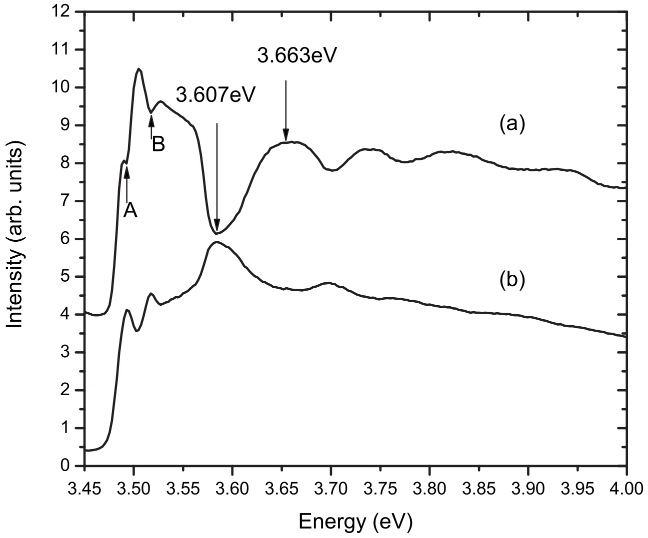

FIG. 2. Photoluminescence excitation spectra recorded at a temperature of 6 K by detecting (a) on the high energy (2.988 eV) side of the photoluminescence spectrum and (b) on the low energy (2.883 eV) side of the spectrum. The numerical quantities of photon energy indicated are those that were determined using scattered light as described in the text. The spectra are offset for clarity.

Using the spectrum in Fig. 2(a) as a reference we turn our attention specifically to the assignment of the broad features in the PLE spectra. There is a great deal of similarity between our spectra and those reported in the work we discussed in the Introduction where the LO phonon assisted excitation of electrons at $k=0$ was discussed. On this basis, we assign the minima or maxima at 3.607 eV, 3.710 eV, 3.802 eV, and 3.893 eV as involving the LO phonon assisted excitation of electrons at $k=0$. We cannot use Eq. (1) to confirm the assignment as we must take into account that the valence band in bulk GaN is split into nonparabolic heavy

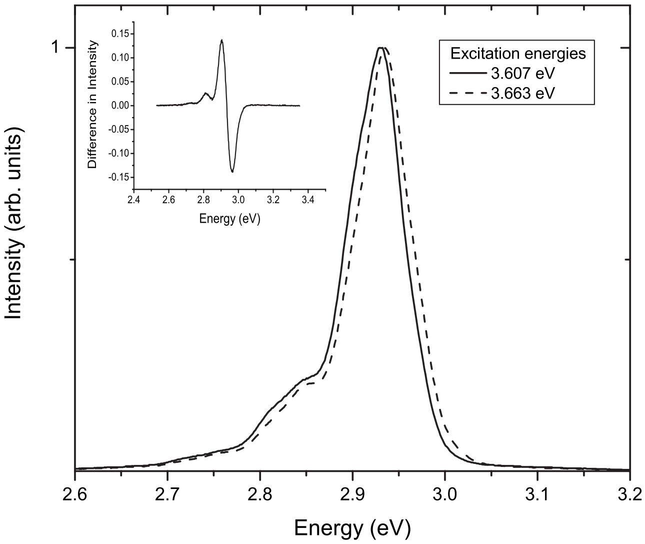

FIG. 3. Photoluminescence spectrum of InGaN/GaN quantum well measured at a temperature of 6 K with the excitation photon energies indicated in the figure legend. In the inset is plotted the spectral dependence of the difference in intensity of the two spectra.

hole, light hole, and crystal field split off bands.[10] Using a value[11] for the effective mass for an electron in the conduction band of GaN of $0.2m_0$ and assuming a parabolic conduction band, the values of k for which the emission of n LO phonons would lead to the scattering of an electron to $k=0$ are given by $\sqrt{n}0.069$ Å^{-1}. Thus using these values of k and by comparing the energies of the dips in the PLE spectrum in Fig. 2(a) with the results of calculations for the valence band structure by Ren *et al.*[10] and using a value[11] for the fundamental band gap of GaN of 3.503 eV (it should be noted that the precise value used for the band gap does not significantly affect our analysis) we are able to confirm our assignment. In particular, the specific minima or maxima identified earlier coincide with the photon energies required for excitation of electrons from the heavy hole valence band and the subsequent LO phonon assisted scattering to $k=0$. It is not clear why we do not see distinct features associated with the light hole valence band but it may be because of the weaker absorption[12] of light via this excitation route. Also as we would expect the light hole transitions to lie only ~20 meV above the heavy hole transitions they may be responsible for the distinct asymmetry on the high energy side of the broad maxima or minima. Next we turn our attention to the sharp features *A* and *B* in Fig. 2. In this spectral region we might anticipate seeing the effects of the direct excitation of electrons at $k=0$ by excitation from the heavy hole and light hole and split off valence bands. The band gaps[10,13] involving these valence bands in unstrained GaN are 3.503 eV, 3.509 eV, and 3.529 eV, respectively. In practice, we see only two sharp maxima or minima in the PL intensity at 3.495 and 3.530 eV. We tentatively assign these features to be the excitation of electrons near to $k=0$ from heavy or light hole (unresolved) and split off valence bands, respectively. It is unlikely that the quoted energies exactly equal the relevant band gaps as at such energies the absorption of light would be vanishingly small for the particular energy gaps involved; also there may be strain effects that would modify the relevant band gaps. At this point in the discussion it is worth commenting on any exciton involvement in the excitation spectra of the quantum well. On superficial examination of the spectra in Fig. 2 it may appear that exciton creation in the barrier does play a role. But based on the interpretation of the peaks provided above we do not need to invoke any distinct exciton transitions, this is in line with the work of Trautman *et al.*[14] who did not resolve any exciton peaks in the GaN absorption spectrum when the GaN was grown at a similar temperature to our barrier layers.

This brings us to the critical question of why the PL spectrum shifts to lower energies when the sample is excited with light of certain critical photon energies that are at or above the GaN band gaps. As discussed earlier similar oscillations were reported by Ambrazevicius[5] in the PLE spectrum of an InGaAs/GaAs single quantum well located 200 nm below the sample surface. They attributed the oscillations to the effect of the surface field producing a very rapid transfer of a non thermalized electron population into the quantum well. It is likely that this mechanism is also responsible for the oscillations reported here, although we believe that specific details of the mechanism are not the same. As the quantum well is only 10.3 nm from the surface we expect that carriers excited in the barriers of the quantum well will be subject to the effects of a strong surface electric field.[15] In the work of Ambrazevicius[5] the dominant mechanism responsible for the observation of the oscillations was the energy dependence of the non-thermalized electron collection efficiency and/or the electron capture rate. In our case if the excitation energies responsible for producing the electrons at $k=0$ resulted in an enhanced carrier capture rate a greater population of electrons in the quantum well would be produced. This if anything would result in a shift of the spectrum to higher energies due to screening of the internal electric field. This is opposite to what we observe. To back up this conclusion we performed PLE measurements at a factor of 30 less excitation power density than those shown in Fig. 2 and observed no change in the PLE spectra.

It is widely accepted that the emission is due to recombination involving localized electrons and holes, although the precise nature of the localization sites is still the matter of debate.[9,16–19] Carriers that are excited in the barrier layers can be distributed across the spectrum of localized states by a combination of processes such as phonon assisted scattering, hopping, and tunneling. Our results suggest that the distribution of carriers amongst the localized states of the quantum well can be influenced by their energy distribution before they are captured in the quantum well. Judging by the width of the zero phonon component of the PL spectrum the electron energies at the different localization centers probably extend over a range in excess of 100 meV. So we propose that the non thermalized electron population could resonantly scatter to a subset of the distribution of localized states by the emission of one or more LO phonons. This would lead to a strengthening of one part of the PL spectrum at the expense of the rest of the spectrum. This we believe is responsible for the shift of the peak energy as shown in Fig. 3. To emphasis this point in the inset of Fig. 3 is shown the intensity difference between the two spectra. In this inset we

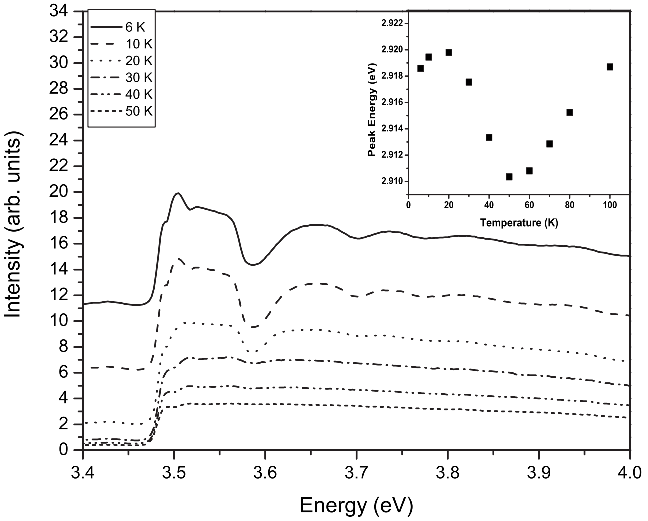

FIG. 4. Photoluminescence excitation spectra recorded at the temperatures indicated by detecting on the high energy side of the photoluminescence spectrum. In the inset is plotted the peak energy of the PL spectrum as a function of temperature. The spectra are offset for clarity.

see that the decrease in integrated intensity on the high energy side is compensated by an increase in the integrated intensity on the low energy side of the spectrum. Note as displayed in the inset the integrated decrease on the high energy side of the zero phonon emission is not equal to the integrated increase on the low energy side. This is because on the low energy side of the spectrum the no phonon and phonon assisted lines overlap. As a further test of this explanation we performed a temperature dependent study of the intensity of the PLE oscillations, the results of which are shown in Fig. 4. As can be seen the oscillations disappear at a temperature of 50 K. Also plotted in the inset of Fig. 4 is a graph of the peak energy of the PL spectrum as a function of temperature. The observed redshift is widely observed in systems where carrier localization occurs[20,21] and is ascribed to the thermally induced redistribution of carriers localized in the higher energy states to the deeper localized states. This shift becomes particularly noticeable at temperatures greater than 20 K, the same temperature at which the PLE oscillations start to be attenuated. This we believe is strong supporting evidence for our suggestion that at low temperatures the form of the low temperature PL spectrum is influenced by the energy distribution of the electrons before they are captured and the mechanism by which the electrons then occupy the localization centers. At the higher temperatures the thermally induced redistribution of the carriers results in a loss of this "memory" effect.

This then begs the following question: Is the so-called *S* shape dependence of the peak energy versus temperature influenced by the excitation photon energy? The comparison of such plots with theoretical predictions has proved[20–22] to be useful in the determination of the energy scale of the potential fluctuations in disordered systems. To investigate this we measured the peak energy of the zero phonon PL spectra as a function of temperature at excitation photon energies of

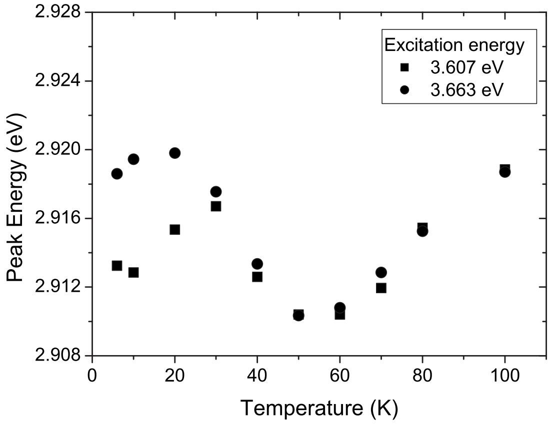

FIG. 5. Photoluminescence peak energy versus temperature for the two excitation photon energies indicated.

3.607 and 3.663 eV (see Fig. 2). The results of these measurements are shown in Fig. 5. Clearly as the temperature is increased to 30 K the peaks of the two sets of spectra behave differently. This is because when the 3.607 eV excitation is used the effect of populating the quantum well with a nonthermalized distribution of electrons is being removed. We believe that this is due to increased thermalization of the electrons before they are captured as the temperature is increased. So it is clear that the form of the plot of the peak energy versus temperature can be a function of the excitation energy but the temperature at which the critical minimum[20] appears is not affected in the system we have studied.

IV. SUMMARY

In summary, we have observed a series of maxima or minima, depending on detection energy, in the PLE spectra of an InGaN/GaN single quantum well that we assign to the resonant excitation of LO phonon and no phonon assisted excitation of nonthermalized electrons. The creation of such a population of electrons causes the PL spectrum to shift in energy which is then responsible for whether the transitions appear as maxima or minima depending on the detection energy. We explain these observations as being due to a modification in the occupation of the distribution of localized states. We have also examined the effects of the electron distribution and have observed a significant modification to the shift of the peak PL energy versus temperature curve.

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