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Mechanism for photoluminescence in an $In_yAs_{1-y}N/In_xGa_{1-x}As$ single quantum well

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Photoluminescence (PL) has been observed in an $In_yAs_{1-y}N/In_xGa_{1-x}As$ single quantum well on InP grown by gas source molecular beam epitaxy at room temperature. The PL spectroscopies show redshift as the nitrogen content increases. Through a detailed study of the dependence of PL spectra on temperature, pumping intensity, and nitrogen content, we point out that the occurrence of PL arises from the localized states due to potential fluctuations induced by the incorporation of nitrogen in InAs. Further evidence is supported by the comparison between the photoconductivity and photoluminescence spectra, which show that the Stokes shift increases with nitrogen content.

I. INTRODUCTION

Low nitrogen content zincblende III-V alloy semiconductors have recently attracted much attention[1–3] due to their interesting physical properties and potential applications of optoelectronic devices. Especially, it leads to the development of technical applications of laser diodes with a wide range of wavelengths. For instance, $In_xGa_{1-x}As_yN_{1-y}$ grown on GaAs substrate is suitable for long-wavelength laser diodes at 1.3 μm,[1,2] and $In_xN_{1-x}As_yP_{1-y}$ grown on InP substrate, for 1.55 μm laser.[3] Both of them are very important for optical fiber communication. In the midinfrared 2–5 μm optoelectronic devices, $In_yAs_{1-y}N$ alloy could be a very promising material. With the advantage of highly strained multiquantum well lasers, it is possible to fabricate good quality material and push the laser emission of $In_yAs_{1-y}N$-based devices to the desired wavelength. However, most of the previous reports were mainly concentrated on the dependence of the $In_yAs_{1-y}N$ band gap on N composition.[4] Studies on the emission property is rather limited. In this paper, we show that the $In_yAs_{1-y}N$ single quantum well can exhibit photoluminescence at room temperature. Based on a detailed study of the $In_yAs_{1-y}N$ quantum wells, we show that the underlying mechanism of the emission can be attributed to the existence of localized states due to potential fluctuations induced by the incorporation of nitrogen in InAs.

II. EXPERIMENT

The samples were grown on semi-insulating (100) In substrates using VG V-80H gas source molecular beam epitaxy system. Element In, Ga, and thermally cracked AsH_3 and PH_3 sources were used. A rf plasma source operated at a radio frequency of 13.56 MHz was used to generate active N species or H species. The rf power for generating N species was 300 W. After the thermal cleaning of the InP substrate at 500 °C under P_2 flux, the brightness mode H_2 plasma was first ignited and a 0.1-μm-thick InP layer was then grown as a buffer layer at 450 °C. Some reports indicated that atomic hydrogen can enhance the removal of surface oxide and passivate some impurities and defects.[5,6] Then, the growth was interrupted and the substrate temperature was reduced to 400 °C for $In_xGa_{1-x}As/InAs(N)/In_xGa_{1-x}As$ single quantum well (SQW) growth. The SQW structure layer is comprised of two 100-nm-thick $In_{0.53}Ga_{0.47}As$ barriers and a 30-Å-thick InAs(N) well. The growth rate for InAs(N) was 1 μm/h. There were no interruptions at the heterointerfaces of the SQW. The gas line of the rf plasma source was switched immediately to N_2 gas when the growth of the first SQW interface began. During the gas switching, the plasma was still maintained at high brightness mode. The rf power was turned off when the growth of the SQW was finished. The beam equivalent pressure (BEP) of the N source during the growth of the $In_yAs_{1-y}N$ SQW was around 10^{-5}–10^{-4} mbar, depending on the nitrogen flow rates. The exact nitrogen content in the $In_yAs_{1-y}N$ SQW was unknown, because the well-thickness is too thin to be determined by x-ray spectrum measurements. Instead of the N composition, we use

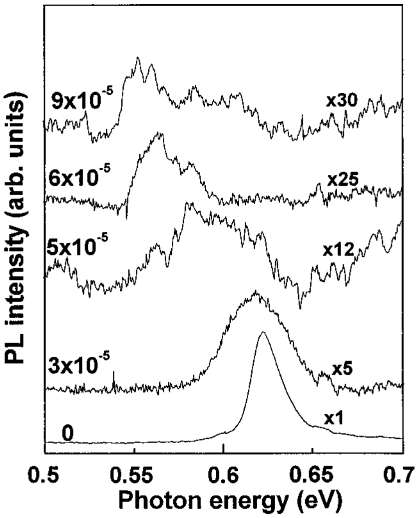

FIG. 1. Photoluminescence spectra of $In_yAs_{1-y}N/In_xGa_{1-x}As$ SQW structures as a function of nitrogen flux at 77 K. The gas pressure is in mbar. The pumping power is 2 W.

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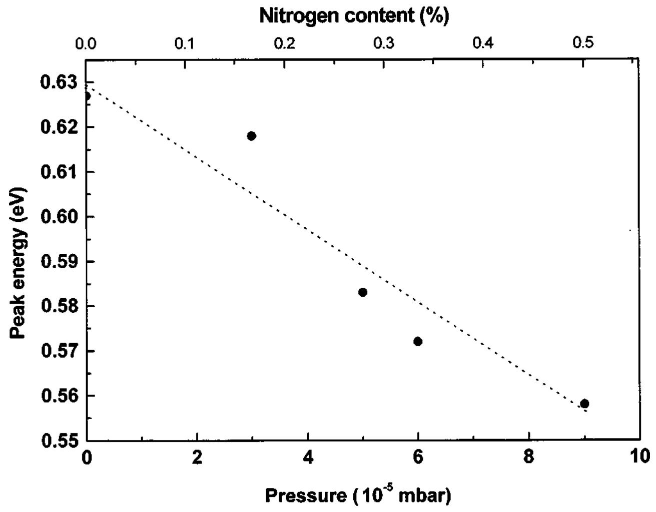

FIG. 2. Dependence of the photoluminescence peak position on nitrogen flux for $In_yAs_{1-y}N$ single quantum wells.

the BEP to divide the different samples. Finally, a 0.1-μm-thick InP cap layer was overgrown on the SQW. It is worth noting that the nitrogen content can be roughly estimated from the photoluminescence (PL) peak position or by assuming that the nitrogen content is linearly proportional to the nitrogen flux.

The photoluminescence measurements were carried out in a liquid-nitrogen-bath cryostat at a temperature of 77 K, in which the varied temperatures ($T = 77-300\,K$) were controlled by an Oxford ITC4 temperature controller. An argon ion laser was used as the pumping source, which was modulated by a mechanical chopper. The luminescence signal was analyzed by a SPEX 500M spectrometer and detected by a liquid-nitrogen-cooled InSb photodiode with a Hamamatsu P3357-02 preamplifier. These detected signals were connected to a lock-in amplifier, and were analyzed by a personal computer. For the photoconductivity (PC) measurement, ohmic contacts were formed by depositing indium drops to the four corners of the samples, and annealing the contacts at 400 °C for 10 s. A tungsten lamp dispersed by a SPEX 500M monochromator was used as the photoexcitation light source. A constant current was supplied to the sample by a Keithley 236 source measure unit. The conductivity signal was detected as a change in the voltage drop across the sample using a lock-in amplifier.

III. RESULTS AND DISCUSSION

The dependence of the $In_yAs_{1-y}N$ SQW PL spectra on nitrogen flow rate is shown in Fig. 1. As can be seen, the PL peak position decreases with increasing nitrogen flux. This indicates a bowing effect of the band gap due to the incorporation of nitrogen in this alloy system. The PL intensity degrades very rapidly with increasing nitrogen concentration. These results indicate the presence of high concentration nonradiative centers. Since there is a very large atomic-size difference between N and As, the large local strain from the nitrogen incorporation in InAs crystal could result in inferior crystallinity. As shown in the previous report for GaPN alloys, the chemical and particularly the size differences between the two anions lead to localized impurity states.[7] Figure 2 shows the dependence of the $In_yAs_{1-y}N$ SQW PL peak energy on the nitrogen flux. The bowing parameter is estimated to be about 15 eV in our samples, if we assume the nitrogen content is linearly proportional to the nitrogen flow rate, and the nitrogen content for the sample deposited with nitrogen flux of 9×10^{-5} mbar is around 0.5%.[8] This value is in good agreement with the low nitrogen content in other III-V compound systems.[9–13] In addition, we have also studied a 0.2-μm-thick $In_yAs_{1-y}N$ sample, which was deposited at a nitrogen flux of 1.9×10^{-4} mbar. From x-ray measurements, the obtained composition of N is 1.06%. If we assume that the nitrogen composition is linearly proportional to nitrogen flux, the estimated nitrogen content for the sample deposited with the nitrogen flux of 9×10^{-5} mbar is 0.5%. It is consistent with the value obtained from the PL peak position. This result thus provides the justification for the fact that the nitrogen content can be roughly estimated from the nitrogen flux. We therefore include the estimated nitrogen content in Fig. 2.

Figure 3 shows the temperature dependence of photoluminescence spectra of the $In_yAs_{1-y}N$ SQW with nitrogen flux of 3×10^{-5} mbar. The redshift of the PL maximum position when temperature increases from 77 to 300 K is about

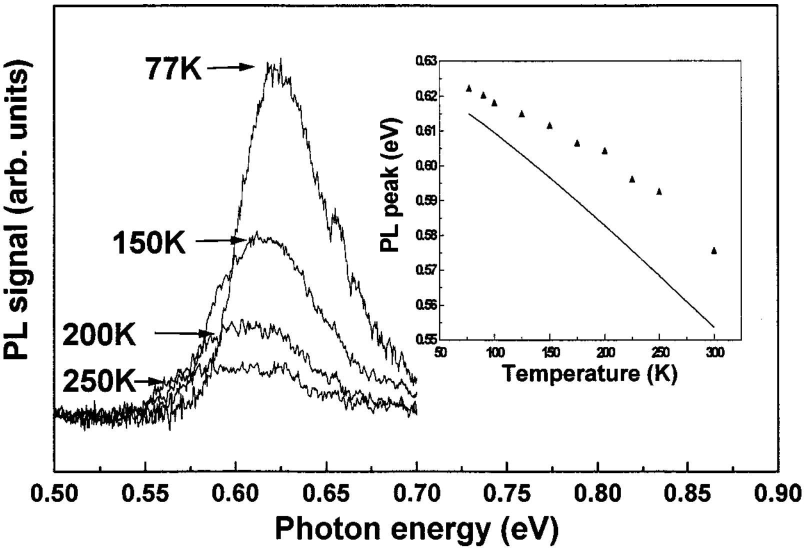

FIG. 3. Temperature-dependent photoluminescence spectra of an $In_yAs_{1-y}N$ single quantum well deposited with nitrogen flux of 3×10^{-5} mbar. The excitation power is 2 W. The inset shows the temperature dependence of photoluminescence peak position. The solid line is the result of Eq. (1) by using InAs thermal coefficients.

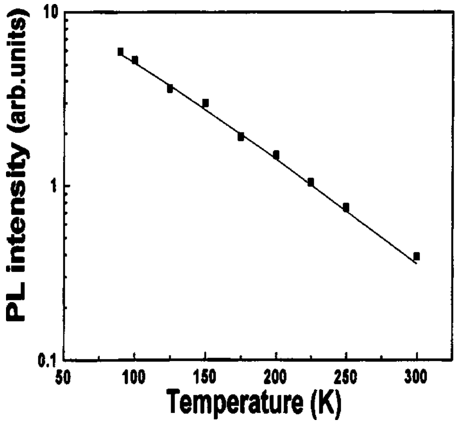

FIG. 4. Temperature dependence of the photoluminescence integrated intensity. The pumping power is 2 W.

50 meV. The energy gap of InAs varies about 65 meV in the same temperature range. This smaller redshift of the $In_yAs_{1-y}N$ SQW indicates that the carriers are thermalized from localized states. The thermalization of carriers from localized states with lower energy to higher energy will retard the decrease of the PL peak position against temperature. For comparison, we also plot the theoretical calculation by using the Varshi equation, which gives the temperature dependence of the energy gap of a semiconductor[14]

$$E(T)=E(0)-\alpha T^2/(\beta+T), \tag{1}$$

where $E(0)$ is the energy gap at $T\sim0$ K; α and β are thermal coefficients. The solid line is obtained by calculating Eq. (1), in which the thermal coefficients of InAs were used for the values of α and β. As expected, the experimental data show a much weaker temperature dependence than theoretical prediction. In addition, this significant character exhibits the broadening on the high-energy side in the PL spectra.[15]

Figure 4 shows the temperature dependence of the PL intensities of the $In_yAs_{1-y}N$ SQW with the lowest nitrogen content. It appears that the data cannot be fitted by an Arrhenius plot. Instead, the temperature dependence is similar to the relationship used for amorphous semiconductors and disordered superlattices[16]

$$I_{PL}=\frac{I_0}{1+A\exp(T/T_0)}, \tag{2}$$

where I_{PL} is the PL intensity, T is the measured temperature, T_0 is the characteristic temperature corresponding to the energy depth of localized states, A is the tunneling factor, and I_0 is the PL intensity at the low-temperature limit. The solid line is the fitting of Eq. (2). The fitting value of A is 0.02, and T_0 is 85 K. Due to the existence of localized states, Eq. (2) has been used to describe the PL behavior in many different disordered system,[16–18] therefore, it seems reasonable to infer that the localization of carriers at band edge due to potential fluctuations may occur in $In_yAs_{1-y}N$ SQW structures. The value of the characteristic temperature T_0 indicates that the energy depth of localized states is about 7 meV. This value is consistent with the amount of the redshift of the PL peak with respect to that of the InAs quantum well. This result implies that the PL quenching is due to the thermal excitation of carriers from localized states into the InAs region.

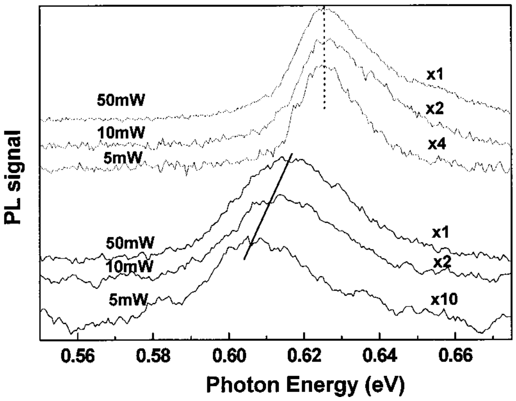

FIG. 5. Excitation power dependence of photoluminescence spectra of $In_yAs_{1-y}N$ SQW structures. The dashed line is for the sample without nitrogen incorporation. The solid line is for the sample deposited with nitrogen flux of 3×10^{-5} mbar.

Additional evidence of the existence of localized states due to potential fluctuations is provided by the measurement of the dependence on the excitation intensity of the PL spectra as shown in Fig. 5. In Fig. 5, we also show the pumping power dependence on the PL spectra for the sample without nitrogen incorporation. It is quite interesting to note that a blueshift of the PL peak energy is observed for the $In_yAs_{1-y}N$, SQW while that of the InAs SQW remains fixed. The blueshift with increasing pumping power cannot be explained in terms of sample heating, which would result in a redshift. This PL behavior is usually considered as evidence for a strong effect of localized states on radiative recombination. The presence of random fluctuations in alloy materials can cause a smearing of band edges and the formation of tails in the density of states extending into the band gap.[19–21] These localized states of band-edge fluctuations are limited in number and are easily filled by the photoexcited carriers. Increasing excitation power will increase the state filling within the band tails; thus, the emission exhibits a blueshift with increasing excitation intensity.

According to the above discussion, if the localized states are due to potential fluctuations induced by the incorporation of nitrogen in InAs, we shall expect that there exists a Stokes shift in the $In_yAs_{1-y}N$ SQW and the magnitude of the Stokes

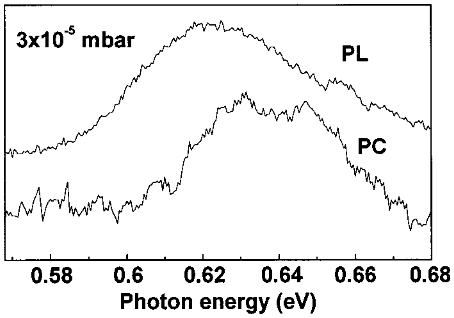

FIG. 6. Photoluminescence and photoconductivity spectra of an $In_yAs_{1-y}N$ single quantum well deposited with nitrogen flux of 3×10^{-5} mbar.

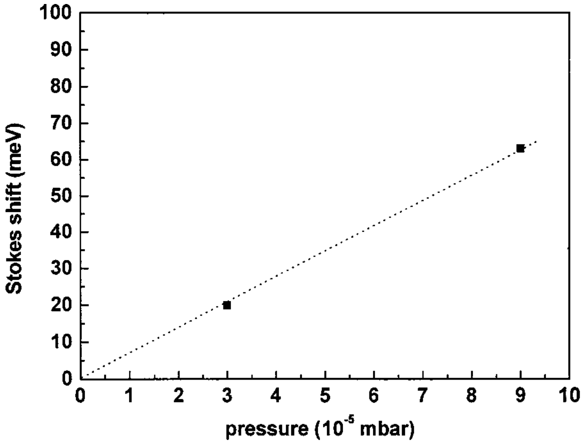

FIG. 7. Dependence of the Stokes shift of $In_yAs_{1-y}N$ single quantum wells on nitrogen flux. Line is a guide for eye.

shift should increase with nitrogen content. As shown in Fig. 6, there indeed exists a Stokes shift of about 20 meV for the $In_yAs_{1-y}N$ SQW deposited with 3×10^{-5} mbar nitrogen flux. This value is larger than $\frac{1}{2}kT$, where k is the Boltzmann constant and T is the absolute temperature, and it cannot be explained by the thermal distribution of carriers. In addition, we also found that the Stokes shift increases with increasing nitrogen content as shown in Fig. 7. It is interesting to note that the extension of the experimental data passes through zero point where the SQW contains no nitrogen. It implies that there is no Stokes shift for the sample without nitrogen incorporation. Therefore, we believe that the observed PL here does arise from the localized states due to potential fluctuations induced by the incorporation of nitrogen.[22]

Finally, even though we show here that the emission of the $In_yAs_{1-y}N$ SQW arises from localized states, the origins of localized states are still undetermined. It is possible that the localized states can simply be attributed to the random nature of the $In_yAs_{1-y}N$ alloy similar to other alloy systems. It can also be due to the large differences in atomic sizes and electronegativities of N and As, which cause the phase segregation in $In_yAs_{1-y}N$ alloys. As a result, it leads to the formation of highly inhomogeneous material with inclusions of InAs and InN phases, similar to the $Ga_xAs_{1-x}N$ alloy system,[23] and thus the existence of potential fluctuations in the studied materials.

In one of our previous studies,[8] we have shown that after rapid thermal annealing (RTA), the PL intensity of the $In_yAs_{1-y}N$ quantum wells is enhanced, the linewidth becomes narrow, and the PL peak is blueshifted. This behavior can be explained quite well by the existence of the formation of inhomogeneous InAs and InN phases in the $In_yAs_{1-y}N$ quantum wells. It is possible that due to the RTA treatment, the N-As interdiffusion between the InAs and InN phases in the well layer can easily occur. This process leads to an improved uniformity of the quantum wells, hence the localization depth and the PL linewidth are redued, the PL peak is blueshifted, and the PL intensity is increased.

IV. CONCLUSION

In summary, we report a detailed study of the PL spectra in $In_yAs_{1-y}N$/GaAs SQW structures grown by gas source molecular beam epitaxy. Based on the dependencies on temperature, pumping power, and nitrogen content, we point out that the occurrence of the PL in the investigated $In_yAs_{1-y}N$ SQW structures can be attributed to the recombination of excitons trapped by localized states due to potential fluctuations induced by the incorporation of nitrogen. Additional evidence of the existence of the localized states is provided by the fact that a large Stokes shift exists between the PL and PC spectra. The occurrence of the N-As interdiffusion inferred from rapid thermal annealing implies that the origin of the localization can be attributed to the formation of InAs and InN phases in the well layer. The result obtained here not only can be used to interpret $In_yAs_{1-y}N$ quantum wells, it may be extended to explain the emission behaviors in other nitride alloys.

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