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Time and Temperature Dependence on Rapid Thermal Annealing of Molecular Beam Epitaxy Grown $Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ Quantum Wells Analyzed Using Photoluminescence

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GaInNAs has received a great deal of attention among the scientific community, owing to its ability to be grown pseudomorphically on GaAs substrates and, thus, to extend the possibility of using GaAs based materials for technologically important wavelengths such as 1.3 μm. Annealing was found to be a very useful tool in improving the optical characteristics of as-grown GaInNAs films. This work presents a systematic statistical analysis of two annealing parameters, time and temperature, for $Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ quantum wells. Annealing, in general, has resulted in decreasing the emission wavelength by at most 0.08 μm, narrowing the peaks by at most ~25 meV and increasing the intensity by at most 90 times. However, from the statistical analysis, it is observed that the temperature is the dominant factor among time and temperature in recovering the optical properties.

Key words: GaInNAs, annealing, photoluminescence, quantum wells, temperature, time, MBE

INTRODUCTION

Since 1995, nitrogen-bearing GaAs materials have attracted a lot of attention owing to their ability to be grown pseudomorphically on GaAs substrates and their type-I band lineup with GaAs.[1] Nitrogen provides two important advantages, huge band-bowing and tensile strain when incorporated in the GaAs lattice, as opposed to compressive strain caused by incorporating indium in GaAs. The strain compensation provided by nitrogen to GaInNAs films was exploited to grow $Ga_{1-x}In_xN_yAs_{1-y}$ ($x \sim 3y$) films that are lattice matched to GaAs substrates. These structures with 8% indium and 3% nitrogen are used in making solar cells at 1 eV.[2] Good optical performance at 1.3 μm was achieved by changing the indium content to 30% and nitrogen to 1% in the films.[3]

Thermal annealing of as-grown GaInNAs films prepared using plasma-assisted molecular beam epitaxy (MBE) have demonstrated a dramatic indium content-dependent recovery of their optical properties.[4–7] An optimum annealing temperature for GaInNAs films was found to be inversely related to indium concentration in quantum well structures.[8] Anneal time is another factor that influences the optical properties. Longer times or higher temperatures are detrimental for annealing owing to increased atomic diffusion and arsenic desorption from the surface. A systematic study of this nature for solid source MBE-grown GaInNAs structures has not been previously explored. This article deals with the statistical analysis performed on annealing properties of $Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ films for two factors, time and temperature, to determine the dominant factor in the annealing process.

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EXPERIMENT

The $Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ films were grown on (100) GaAs substrates using plasma-assisted MBE in a Varian Gen II MBE system equipped with an EPI UniBULB™ (VEECO–Applied EPI, Inc., St. Paul, MN) plasma source. The system uses a gas mixture comprised of nitrogen and argon gas as the nitrogen source; solid sources for Ga, In, and Al; and a valved arsenic cracker for arsenic flux.[9] A gas flow rate of 0.6 sccm and plasma power of 300 W were used for growing all the films. The structure is comprised of triple quantum wells, which are 7-nm thick, surrounded by 15-nm-thick GaAs barriers. Two 150-nm AlAs layers were grown on both sides of the active region to provide optical confinement for the carriers. The quantum wells and barriers were grown at 480°C and the rest of the layers were grown at 580°C. Annealing was performed at four different temperatures, 750°C, 850°C, 900°C, and 950°C, and three different times, 20 sec, 60 sec, and 100 sec. An additional combination of 850°C and 180 sec was also chosen. The annealing was done in nitrogen ambience using an AG Associates rapid thermal annealer. The samples were placed face down on a GaAs sample to compensate for loss of arsenic from the samples at higher temperatures. Ramp rates of 50°C/sec were employed for ramp up and the temperature was ramped down from anneal temperature to less than 300°C in less than a minute. Photoluminescence properties were measured at room temperature using a 488-nm Ar^+ line, SPEX 1704 1-m spectrometer, and a liquid nitrogen-cooled Ge detector. The sample was diced into 13 pieces and each of the pieces was used for one time-temperature combination. Preanneal and postanneal photoluminescence measurements were performed on each piece.

The results were analyzed using Origin v6.1 (OriginLab Corp., Northampton, MA) for determining the peak properties and the results were normalized to unannealed $Ga_{0.8}In_{0.2}As$ properties. The postanneal measurements were measured relative to preanneal measurements to obtain the annealing properties such as decrease in wavelength and FWHM in addition to improvements in integrated intensity, at the respective time-temperature combinations. These annealing properties were further analyzed using the statistical software JMP (Sas Institute, Cary, NC) 4.0 to determine the dominant factor among time and temperature and to obtain an optimum-annealing situation based on desirable wavelength, full-width at half-maximum (FWHM), and integrated intensity.

RESULTS AND DISCUSSION

Rapid thermal annealing is a popular method used for recovering the damage caused to GaInNAs films.[6] In this article, the optical properties of annealed GaInNAs quantum wells, namely, emission wavelength, FWHM, and integrated intensity are analyzed. Figure 1 shows the general trends in the annealing properties. For increases in either anneal time or temperature, the emission wavelength blue-shifts, FWHM initially decreases as a result of enough thermal energy being present to overcome the activation energy of the damage, and then it ultimately increases as diffusion dominates, which is consistent with the results seen by others.[8] The integrated intensity increases as anneal time or temperature increases. Thus, time and temperature are expected to complement each other in determining the optical properties. There is evidence of a temperature threshold required for observing a measurable impact on the properties and a saturation or deterioration of properties at high temperatures.

The emission wavelength blue-shifts (20–800 Å) with an increase in anneal time for temperatures of 750°C or greater, and blue-shifts as temperature increases for any anneal time, as shown in Fig. 1a and b. We believe that the blue-shift is related to out-diffusion of indium from the quantum wells. A temperature threshold ($T \geq 750°C$) is required before any significant blue-shift in the wavelength is observed; this effect continues as the temperature increases. Therefore, temperatures less than 750°C are not discussed in this article.

The FWHM does not change for shorter times and low temperatures, as shown in Fig. 1c and d. It then decreases initially (~20 meV) as time or temperature increases, i.e., peaks narrow as time or temperature increases. However, on supplying enough thermal energy, we believe that diffusion becomes dominant to counteract the damage recovery due to annealing. This results in eventual broadening of the peaks (~−25 meV) with further increase in time or temperature. In addition, at higher temperatures, it requires lesser time for the peak broadening to set in.

The integrated intensity increases (0.5–90×) as annealing removes the damage caused to GaInNAs films. This process should require a minimum thermal energy for the onset of recovery. The integrated intensity recovery is related to removal of traps that were introduced by plasma-related damage.[4] This annealing recovery, however, is limited. The additional energy that is present after removing the plasma-related damage when annealed for longer times or at higher temperatures results in desorbing arsenic from the GaAs surface. This desorption manifests itself as a saturation of the integrated intensity when annealed for longer times or a decrease in integrated intensity improvement for anneal temperatures greater than 900°C. As shown in Fig. 1e and f, for integrated intensity plotted against time, less time is required at higher temperatures to initiate the recovery process and to saturate the integrated intensity owing to the complementary contribution of time and temperature. These results show that it is imperative that a statistical analysis for determining the optimum time-temperature combination be used to optimize the annealing process.

These results are analyzed using the statistical software JMP 4.0. The factorial design technique is implemented to choose the time-temperature combinations in order to determine the dominant factor for each of the annealing properties.[10] The significance of the variable for the predicted model is determined by calculating the "Prob $> |F|$" parameter, a probability less than 0.05 being a significant variable, a probability slightly greater than 0.05 being a borderline variable, and a probability greater than 0.05 being an insignificant variable. Table I shows the significant variables influencing the properties and predicted ideal time-temperature combinations based on their individual desirabilities. From Table I, it is

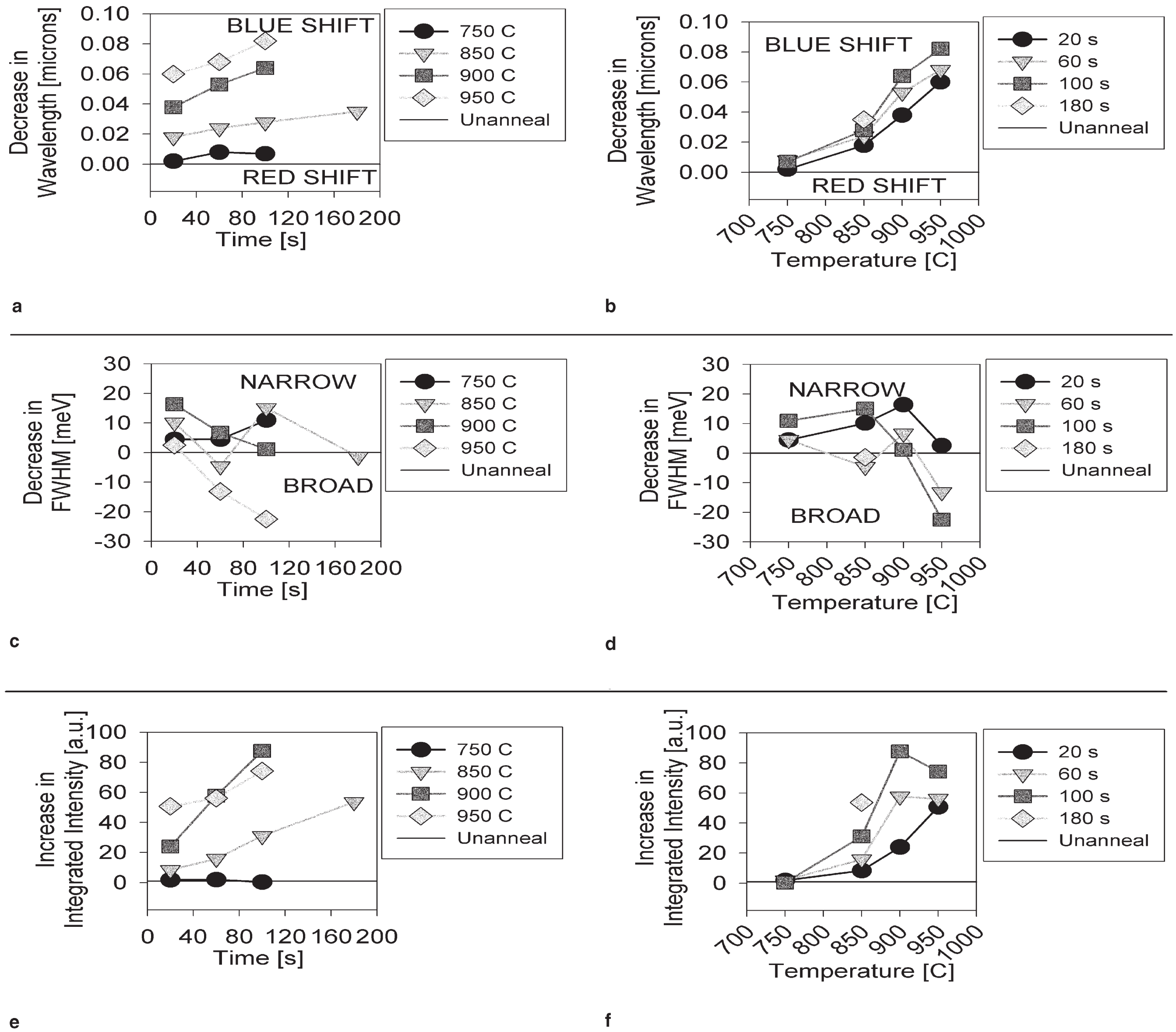

Fig. 1. (a)–(f) Annealing properties of GaInNAs quantum wells.

seen that the temperature and its derivatives are the most significant variables for three optical properties and time is the next important variable, since it has borderline significance for decreasing FWHM. Figure 2 shows the predicted decrease in wavelength, decrease in FWHM, and increase in integrated intensity as a function of time and temperature.

The model can be used to maximize the desirability of each parameter. For the best annealing conditions, it is desired that the decrease in wavelength is minimum and the decrease in FWHM is maximum. Integrated intensity measures both FWHM and intensity. Annealing is expected to increase the luminescence intensity by removing the traps and to reduce the FWHM. Since these have opposing effects on integrated intensity, the most desirable condition for integrated intensity is to remain constant. This is represented as the “Match Target” option in JMP 4.0 software.

Based on these desirabilities, the model predicts that annealing should be performed for shorter periods of time at lower temperatures for minimum loss in emission wavelength. Longer times or higher temperatures, as shown in Fig. 1, are observed to demonstrate greater blue-shift, suggesting that the time-temperature combination that is predicted by the model is reasonable for minimizing the decrease in emission wavelength.

On the other hand, the model predicts that annealing should be performed for longer periods of time at lower temperatures to obtain maximum decrease in FWHM. As shown in Fig. 1c and d, it is observed that sufficient thermal energy is required before significant reduction in FWHM is seen. However, we believe that diffusion becomes the dominant factor for annealing performed at conditions with high thermal energies provided by increasing the temperature. Based on these observa-

Table I. Fit Results and Ideal Annealing Conditions Based on Individual Desirability

Parameter	R^2	R_{adj}^2	Model: Variables Used	Model: Prob > $\lvert F \rvert$	Influence on the Parameter	Desirability	Predicted Ideal Conditions
Decrease in wavelength	0.95	0.93	T	<0.0001	Significant	Minimize	750°C, 20 sec
			t	0.0116	Significant		
			T^2	0.0130	Significant		
Decrease in FWHM	0.72	0.59	T	0.0047	Significant	Maximize	750°C, 180 sec
			t	0.0504	Borderline		
			T^2	0.0323	Significant		
			T and t	0.0441	Significant		
Increase in integrated intensity	0.81	0.77	T	0.0002	Significant	Match target	918.02°C, 92.462 sec
			t	0.0131	Significant		

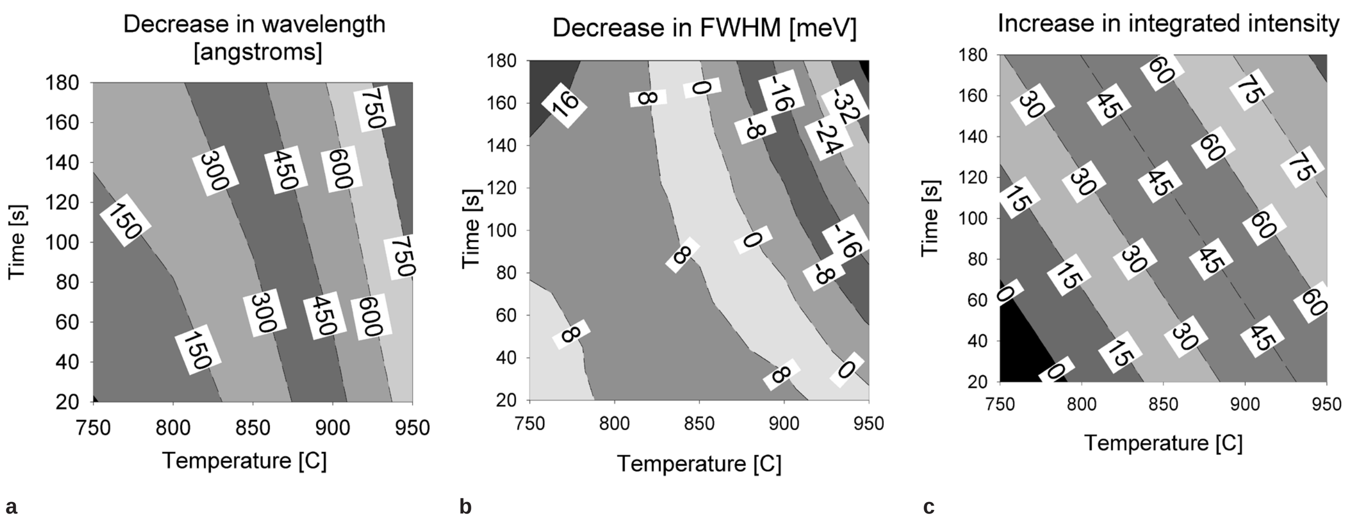

Fig. 2. Predicted profiles for the decrease in emission wavelength, decrease in FWHM, and increase in integrated intensity as a function of annealing temperature and annealing time.

tions, annealing performed for longer times at low temperatures, as predicted by the model, will yield maximum reduction in FWHM.

According to the model, annealing should be performed at moderate amounts of time for moderately high temperatures to keep the integrated intensity constant. The increase in intensity is very small for those samples that were annealed at low temperatures, and the peaks broaden for larger annealing temperatures or for longer anneal times. Hence, a suitable combination of moderate times (~100 sec) with moderately high temperatures (~900°C) is expected to yield the best results with improving the intensity and reducing the FWHM.

The amount of thermal energy that is required to recover the optical properties depends on the defects that are present in the epitaxial layers. The amount of indium present in the quantum well is one of the parameters that determine the defect concentration. As the defect concentration increases, lower thermal energies are required to onset the annealing process, when compared to quantum wells with 20%In.[8] Hence, the optimum anneal condition for quantum wells with ~30%In is expected to be at lower thermal energy.

CONCLUSIONS

It is observed that temperature is the most dominant factor in determining the annealing effects of GaInNAs quantum well structures. Annealing, in general, has resulted in decreasing the emission wavelength, reducing FWHM of peaks and increasing the integrated intensity. From the statistical analysis, it is determined that the optimum annealing condition for $Ga_{0.8}In_{0.2}N_{0.01}As_{0.99}$ quantum wells with GaAs barriers depends on the response variable. In order to obtain the minimum decrease in wavelength, annealing needs to be performed at lower temperatures for shorter times. Similarly, for a maximum decrease in FWHM, the optimum annealing condition is at low temperatures and longer times, and for best-integrated intensity, the optimum annealing condition is at moderately high temperatures and moderate times.

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