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Correlation of electrical and optical properties in dually Cd$^+$ and N$^+$ ion-implanted GaAs

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Abstract

Cd in GaAs is an acceptor atom and has the largest atomic diameter among the four commonly-used group-II shallow acceptor impurities (Be, Mg, Zn and Cd). The activation energy of Cd (34.7 meV) is also the largest one in the above four impurities. When Cd is doped by ion implantation, the effects of lattice distortion are expected to be apparently different from those samples ion-implanted by acceptor impurities with smaller atomic diameter. In order to compensate the lattice expansion and simultaneously to adjust the crystal stoichiometry, dual incorporation of Cd and nitrogen (N) was carried out into GaAs. Ion implantation of Cd was made at room temperature, using three energies (400 keV, 210 keV, 110 keV) to establish a flat distribution. The spatial profile of N atoms was adjusted so as to match that of Cd ones. The concentration of Cd and N atoms, [Cd] and [N] varied between 1×10^{16} cm^{-3} and 1×10^{20} cm^{-3}. Two type of samples, i.e., solely Cd$^+$ ion-implanted and dually (Cd$^+$ + N$^+$) ion-implanted with [Cd] = [N] were prepared. For characterization, Hall effects and photoluminescence (PL) measurements were performed at room temperature and 2 K, respectively. Hall effects measurements revealed that for dually ion-implanted samples, the highest activation efficiency was ~ 40% for [Cd] (= [N]) = 1×10^{18} cm^{-3}. PL measurements indicated that [g–g] and [g–g]$_i$ (i = 2, 3, α, β, ...), the emissions due to the multiple energy levels of acceptor-acceptor pairs are significantly suppressed by the incorporation of N atoms. For [Cd] = [N] $\geq 1 \times 10^{19}$ cm^{-3}, a moderately deep emission denoted by (Cd, N) is formed at around 1.45–1.41 eV. PL measurements using a Ge detector indicated that (Cd, N) is increasingly red-shifted in energy and its intensity is enhanced with increasing [Cd] = [N]. (Cd, N) becomes a dominant emission for [Cd] = [N] = 1×10^{20} cm^{-3}. The steep reduction of net hole carrier concentration observed for [Cd]/[N] ≤ 1 was ascribed to the formation of (Cd, N) which is presumed to be a novel radiative complex center between acceptor and isoelectronic atoms in GaAs.

1. Introduction

A great deal of systematic impurity doping studies have been carried out to understand the mechanism of dopant incorporation into GaAs. We have recently demonstrated that when acceptor impurities such as group II (Be, Zn, Cd and Hg) and IV(C) elements are introduced into GaAs by carefully suppressing the incorporation of shallow donor impurities, their optical properties particularly low-temperature photoluminescence (PL) spectra present totally dissimilar features to the well-documented reports [1–4]. In the 2 K PL spectra, specific emissions inherent to isolated

and pairing acceptor impurities can be routinely observed slightly below the conduction band–acceptor level transition, (e, A).

Cd in GaAs holds an activation energy of 34.7 meV and is a moderately deep acceptor impurity. One should notice that the atomic radius of Cd is greater than that of Ga and As. It is accordingly considered that when Cd is incorporated by high-energy ion implantation with relatively high dose, dual ion implantation of Cd atoms and group V elements with smaller atomic radius is an appropriate method to suppress lattice expansion and simultaneously to maintain stoichiometry [5]. Since nitrogen (N) has a smaller atomic radius than host Ga and As atoms, the lattice expansion of GaAs due to Cd incorporation is expected to be negated by dual implantation with N$^+$ ions. In this paper we present optical and electrical properties of

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GaAs implanted with $Cd^+ + N^+$ ions and compare them with those of singly Cd^+ or N^+ ion-implanted samples.

2. Experimental

It was explicitly demonstrated that optical properties, particularly photoluminescence (PL) spectra are critically dependent upon impurity concentration [4]. When doping is made by high-energy ion implantation, a flat distribution of impurities is accordingly highly desired by using multiple ion-implantation energies. In this experiment we used three different energies of 400, 210 and 110 keV which establish a flat distribution of Cd atoms extending from 0.01 μm to 0.08 μm below the surface that was calculated using LSS theory [6]. The N^+ ions were implanted at the energies of 40 keV and 20 keV in order to match their spatial profile with that of Cd atoms. LEC GaAs substrates with (100) orientation were used for ion implantation. The top flat-part concentration of the two implanted species,
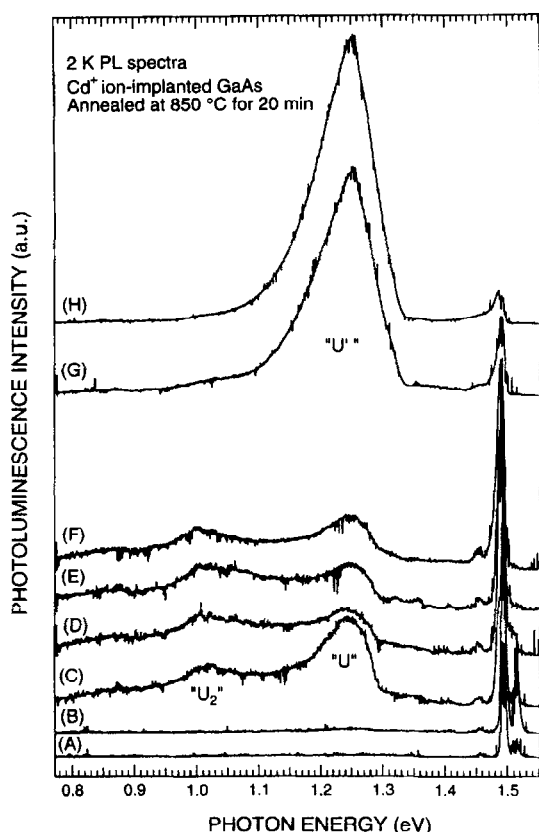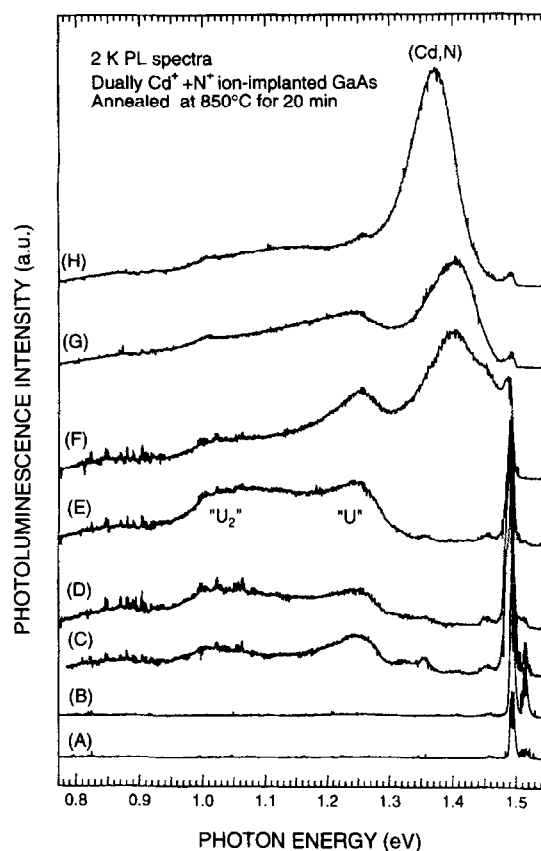
Fig. 2. 2 K PL spectra for dually $Cd^+ + N^+$ ion-implanted GaAs as a function of [Cd] = [N]. Emissions were detected using liquid N_2-cooled Ge detector: (A) virgin GaAs; (B) undoped annealed GaAs; (C) [Cd] = [N] = 1×10^{17} cm^{-3}; (D) 1×10^{18} cm^{-3}; (E) 3×10^{18} cm^{-3}; (F) 1×10^{19} cm^{-3}; (G) 3×10^{19} cm^{-3}; (H) 1×10^{20} cm^{-3}.

[Cd] and [N] was varied from 1×10^{17} to 3×10^{20} cm^{-3} by keeping the relative concentration ratio for [Cd]/[N] at unity. Furnace annealing was made at 850°C for 20 min in 85% Ar and 15% H_2 ambient with a GaAs proximity cap. Low-temperature PL experiments were made at 2 K using an Ar^+ laser (514.5 nm line) with a 1 m monochromator and Ge detector. Hall effect measurements were performed by a standard van der Pauw technique at room temperature.

3. Results and discussion

2 K PL spectra of singly Cd^+ ion-implanted GaAs are illustrated in Fig. 1 as a function of [Cd], in which Ge detector was used. In the figure, several sharp emissions at around 1.50 eV (830 nm), designated by (e, C), (D, C) and (e, Cd) are the emissions due to conduction band–C acceptor, unidentified donor–C acceptor pair and conduction band–Cd acceptor transitions, respectively. (e, C) and

Fig. 1. 2 K photoluminescence (PL) spectra for singly Cd^+ ion-implanted GaAs as a function of Cd concentrations, [Cd]. Emissions were detected using liquid N_2-cooled Ge detector: (A) virgin GaAs; (B) undoped annealed GaAs; (C) [Cd] = 1×10^{17} cm^{-3}; (D) 1×10^{18} cm^{-3}; (E) 3×10^{18} cm^{-3}; (F) 1×10^{19} cm^{-3}; (G) 3×10^{19} cm^{-3}; (H) 1×10^{20} cm^{-3}.

(D, C) are distinctively recognized as emissions derived from residual C (carbon) and unknown donor(s) originally existing in the as-grown LEC substrates [4]. In the undoped both unannealed (Fig. 1A) and annealed (Fig. 1B) GaAs specimens, no appreciable emission is recognized in the energy region ~ 0.8–1.4 eV. Two relatively broad emissions denoted by 'U' and 'U$_2$' situated at ~ 1.26 eV and 1.01 eV, respectively appear when Cd atoms are introduced (Fig. 1C–F). The general spectral features do not change for [Cd] lower than 1×10^{19} cm^{-3}, while for [Cd] larger than 3×10^{19} cm^{-3} (Fig. 1G–H) the intensity and energy half-width of 'U' are significantly enhanced and 'U' becomes the most dominant emission. It is accordingly reasonable to re-designate the emission at 1.26 eV as 'U''' for [Cd] larger than 3×10^{19} cm^{-3}. The intensity of 'U$_2$' on the other hand seems to be not much affected by the increment of [Cd]. It is of great importance to note that 'U''' is not formed in either simply N$^+$ or P$^+$ ion-implanted GaAs, stating that 'U''' is not necessarily associated with defects produced by high-energy ion implantation and successive high-temperature annealing. The results in Fig. 1 are the first experimental demonstration that Cd atoms incorporated by high-energy ion implantation

produce a quite dominant deep emission in the high dose regime [3].

2 K PL spectra of dually Cd$^+$ and N$^+$ ion-implanted GaAs are indicated in Fig. 2 as a function of absolute value of [Cd]($=$[N]) for the same energy region of Fig. 1. For [Cd]($=$[N]) lower than 3×10^{18} cm^{-3}, PL features of dually Cd$^+$ + N$^+$ ion-implanted samples are quite similar to those of singly Cd$^+$ ion-implanted ones. In the figure one notes that for [Cd]($=$[N]) higher than 1×10^{19} cm^{-3}, a moderately deep emission denoted by (Cd, N) is formed at 1.40 eV. This (Cd, N) exhibits a steep energy shift towards lower energy side (red-shift) with increasing [Cd]($=$[N]) and becomes the predominant emission for [Cd]($=$[N]) $= 1 \times 10^{20}$ cm^{-3}. (Cd, N) is not created in simply N$^+$ or Cd$^+$ ion-implanted sample [4,7]. Judging from these results, (Cd, N) can be suggested to be a novel radiative emission closely associated with the pairs between a Cd acceptor atom and a N isoelectronic impurity. It can be accordingly expected that (Cd, N) exhibits a strong dependence of emission energy on the pair separation. The radiative properties relevant to an acceptor-isoelectronic impurity complex were first observed in indirect band-gap GaP as fine-line undulation emissions [8]. The
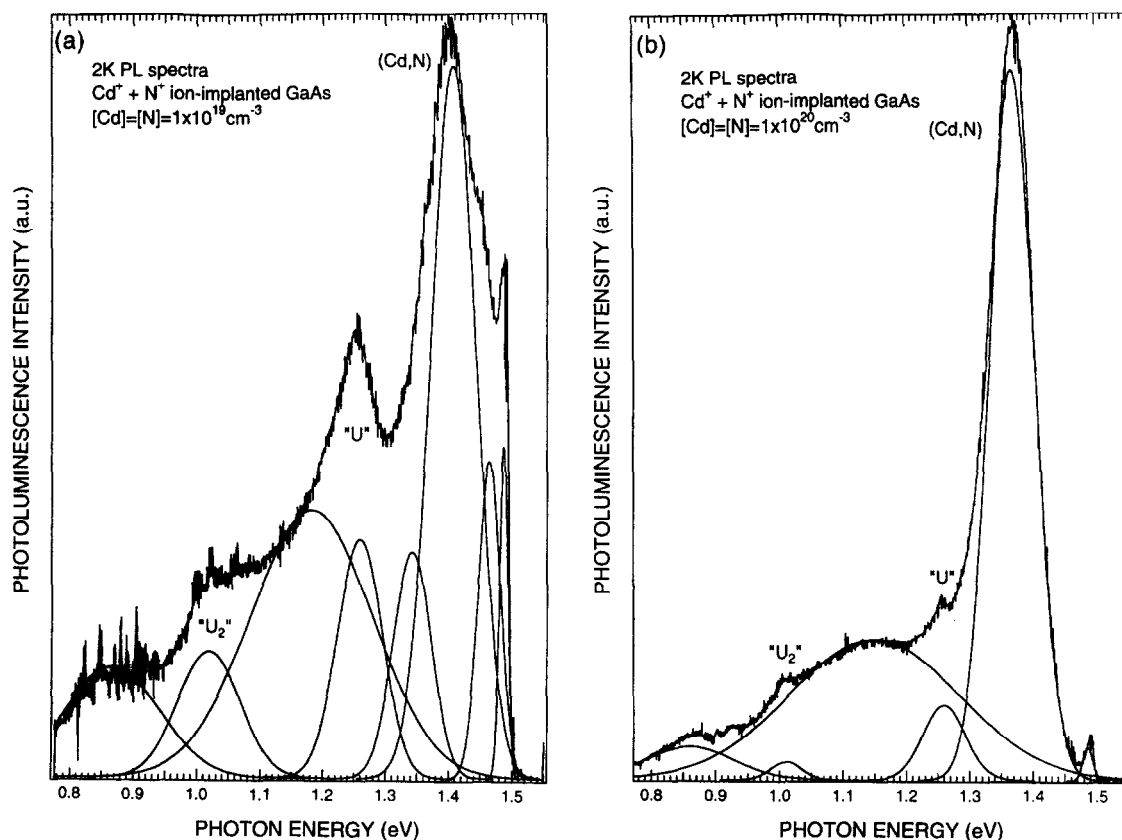

Fig. 3. (A) The results of least square curve fitting to the PL spectrum from dually Cd$^+$ and N$^+$ ion-implanted samples with [Cd]($=$[N]) $= 1 \times 10^{19}$ cm^{-3}. (B) The results of least square curve fitting to the PL spectrum from dually Cd$^+$ and N$^+$ ion-implanted samples with [Cd]($=$[N]) $= 1 \times 10^{20}$ cm^{-3}.

dominant contribution of (Cd, N) and the highly suppressed remaining deep emissions below 1.3 eV for $[Cd](= [N]) = 1 \times 10^{20}$ cm^{-3} suggest that stoichiometry was reasonably adjusted and lattice expansion was fairly reduced by the dual ion implantation of heavy acceptor ion (Cd) and light group V element (N). It is of great importance to note that the 1.3 eV emission can not be quenched by the dual implantation of Cd$^+$ and P$^+$ ions [9].

The intensity variation of the two PL spectra obtained from $[Cd](= [N]) = 1 \times 10^{19}$ cm^{-3} and 1×10^{20} cm^{-3} was analyzed and the individual result is indicated in Fig. 3(A) and (B), respectively. One notices that the relative intensity of (Cd, N) to that of remaining emissions is greatly enhanced and the central emission energy of (Cd, N) is red-shifted with increasing [Cd]. The origin of the two deep emissions located at 0.86 eV and 1.15 eV can not be fully elucidated yet. In the figures, the emission at 1.486 eV is due to (e, Cd) and the emission at 1.464 eV is supposed to be partly associated with the phonon replica of (e, Cd).

Room temperature net hole concentration, $|N_A-N_D|$ of singly Cd$^+$ and dually Cd$^+$ and N$^+$ ion-implanted GaAs samples are presented in Fig. 4. The thickness of the Cd (or +N)-doped layer was obtained from SIMS measurements. In both singly and dually ion-implanted samples, $|N_A-N_D|$ increases with increasing $[Cd](= [N])$ for [Cd] lower than 1×10^{19} cm^{-3}. For [Cd] higher than 1×10^{19} cm^{-3}, the singly Cd$^+$ ion-implanted GaAs specimens present continuously increasing value of $|N_A-N_D|$, while the dually ion-implanted GaAs samples exhibit saturated value of $|N_A-N_D|$. We obtained maximum $|N_A-N_D|$ of 6.3×10^{18} cm^{-3} for singly implanted sample and 2.5×10^{18} cm^{-3} for dually implanted sample at $[Cd](= [N]) = 1 \times 10^{20}$ cm^{-3}. The highest activation efficiency was ~ 40% at [Cd] $(= [N]) = 1 \times 10^{18}$ cm^{-3} for both singly and dually ion-implanted specimens. The results shown in Fig. 4 indicate that the activation rate of the dual ion-implanted sample steeply decreases with increasing $[Cd](= [N])$ particularly for [Cd] higher than 1×10^{19} cm^{-3}. This feature can be ascribed to the formation of moderately deep emission, (Cd, N) that can efficiently annihilate holes produced by the incorporation of Cd acceptor impurities. These results suggest that dual ion implantation of Cd acceptor impurity and extremely light group V isoelectronic atom (N) does not work for enhancing $|N_A-N_D|$ although the introduction of second ions (N$^+$) is effective for the adjustment of stoichiometry and the release of lattice-distortion.

4. Conclusion

Single Cd$^+$ and dual Cd$^+$+N$^+$ ion implantation were carried out for LEC-GaAs substrates at room temperature with high-energy (400 keV). 2 K photoluminescence spectra showed that for Cd concentration, [Cd] lower than
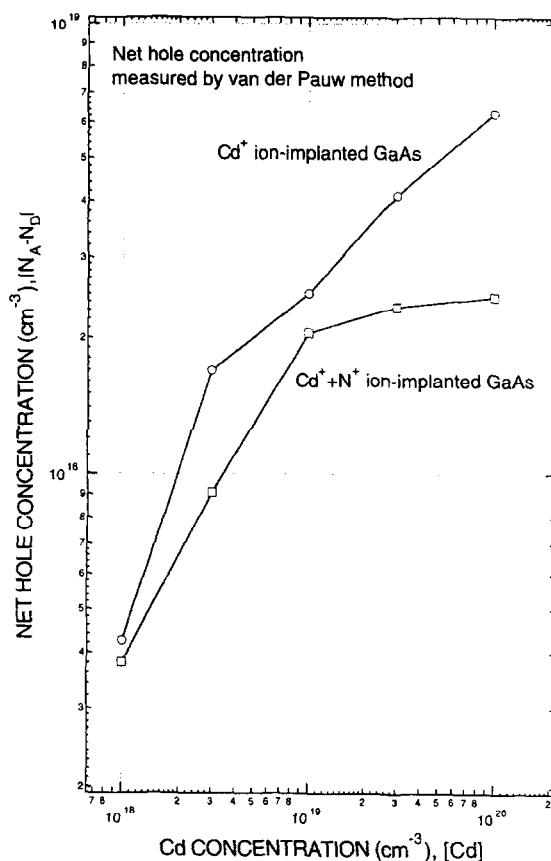

Fig. 4. Net hole concentration, $|N_A - N_D|$ of singly Cd$^+$ and dually Cd$^+$ and N$^+$ ion-implanted samples as a function of $[Cd](= [N])$ measured by van der Pauw method at room temperature.

1×10^{19} cm^{-3}, the well-established conduction band to Cd acceptor emission together with a relatively deep radiative energy levels at 1.0 eV and 1.26 eV was observed for both singly and dually Cd$^+$ ion-implanted samples. For dually implanted samples with $[Cd](= [N])$ higher than 1×10^{19} cm^{-3}, a moderately deep emission temporarily denoted by (Cd, N) was observed at 1.38 eV which presented an energy shift towards lower energy side with increasing $[Cd](= [N])$.

Hall effect measurements performed at room temperature showed that highest $|N_A-N_D|$ of 6.3×10^{18} cm^{-3} and 2.5×10^{18} cm^{-3} were obtained for singly and dually ion-implanted samples at $[Cd](= [N]) = 1 \times 10^{20}$ cm^{-3}. The unexpected low activation rate was ascribed to the formation of the above Cd acceptor–N isoelectronic pair radiative energy level.

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