Spin-dependent recombination in GaAsN alloys

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The spin-dependent recombination (SDR) has been observed in GaAs$_{1-x}$N$_x$ ($x = 2.1, 2.7, 3.4\%$) at room temperature. It reveals itself in a decrease of the edge photoluminescence (PL) intensity by more than a factor of 3 when either the polarization of the exciting light is changed from circular to linear or the transverse magnetic field of $\sim 300$ gauss (G) is applied. The interband absorption of the circularly polarized light results in a spin polarization of conduction electrons, which reaches $35\%$ with increasing the pump intensity. The effects observed are explained by dynamical polarization of deep paramagnetic centers and spin-dependent capture of conduction electrons by these centers. The PL depolarization in a transverse magnetic field (Hanle effect) allows us to estimate the electron spin relaxation time in the range of 1 ns. Theoretically, it has been concluded that, due to the SDR, this long time is controlled by slow spin relaxation of bound electrons. In all the three alloy samples, a positive sign of the bound-electron $g$-factor is determined experimentally from the direction of their mean spin rotation in the magnetic field.

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In recent years Ga(In)AsN alloys grown on GaAs substrates have attracted an increasing interest due to their unusual physical properties and application in near-infrared optoelectronics. The interaction of nitrogen localized isoelectronic states with the conduction-band edges results in an anomalous reduction in the band gap for a small, a few \%, nitrogen content.\cite{1,3,4} Evidently, the understanding of the free-carrier kinetics and recombination mechanisms in these materials are important from the point of view of both fundamental physics and practical applications. In the present work the SDR has been demonstrated in GaAsN alloys for the first time. It manifests itself at room temperature in a strong decrease of the edge PL intensity when the polarization of exciting light is changed either from circular to linear or the transverse magnetic field of $\sim 300$ G is switched on. A high spin polarization ($\sim 35\%$) and long-term spin memory ($\sim 1$ ns) of conduction electrons, both related to the SDR, were observed also at room temperature. We studied the 0.1 \micron thick nominally undoped GaAsN films grown by the MBE on a semi-insulating (001) GaAs substrate between GaAs layers. Arsine was used as the source of arsenic. After the growth, the structures were annealed for 5 minutes at 700\degree C in the flow of arsenic in the growth chamber. Investigated were 3 samples with nitrogen content $x = 2.1, 2.7, 3.4\%$.

The spin polarization of conduction electrons was created under interband absorption of the circularly polarized light.\cite{4} Its magnitude was determined by measuring the degree of PL circular polarization $\rho = (I^+ - I^-)/(I^+ + I^-)$, where $I^+$ and $I^-$ are the intensities of the right ($\sigma^+$) and left ($\sigma^-$) circularly polarized PL components, respectively. A highly sensitive polarization analyzer\cite{5} with an InGaAsP photomultiplier, a quartz polarization modulator, and a two-channel photon counter synchronized with the polarization modulator were used to measure $\rho$ and the total intensity $I = I^+ + I^-$ in a spectral range up to 1.4 \micron. PL was excited by tunable Ti:sapphire laser along the normal to the sample and recorded in the backscattering geometry along the growth axis $z \parallel [001]$. The measurements were carried out at 300 K. As the main experimental results are qualitatively the same for all the samples under study, we present below the data for Ga$_{1-x}$N$_x$ alloy with $x = 2.1\%$.

Fig. 1 shows the PL spectra and circular polarization measured in GaAs$_{0.979}$N$_{0.021}$ sample under excitation by circularly polarized ($\sigma^+$ or $\sigma^-$) light of a high intensity (an increase in $x$ in the samples with $x = 2.7\%$ and $x = 3.4\%$ brings about a strong red shift of the spectra). Each PL spectrum consists of two strongly overlapping bands, their splitting grows with the increasing nitrogen content and reaches 50 meV at $x = 3.4\%$.\cite{8} Relative to the polarization of the pump beam, the low- and high-energy bands are polarized, respectively, negatively and positively. The presence of two PL bands and the opposite signs of their polarization were interpreted in our previous works\cite{6,7} as originating from the strain-induced splitting of the light- and heavy-hole subbands of the complicated valence band $\Gamma_8$. Indeed, the smaller lattice constant of GaAsN as compared with GaAs results in a biaxial tension of the GaAsN film in the interface plane, which is equivalent to a uniaxial compression along the growth axis. The uniaxial strain is accompanied by splitting of light- and heavy-hole subbands, which increases with increasing $x$. The polarization spectrum in Fig. 1 was measured under simultaneous excitation of electrons from the both valence subbands. In order to exclude an excitation of electrons into GaAs barrier, the energy of exciting quanta was smaller than the band gap of GaAs. Thus, the negative polarization of the low-energy PL band and the positive polarization of the high-energy PL band allow one to conclude that those bands arise due to...
the radiative recombination of electrons with light and heavy holes, respectively.

Spectrum 2 in Fig. 1 is obtained under excitation by linearly (π) polarized light. It is seen from curves 1 and 2 that the change of excitation light polarization from circular to linear leads to a decrease of PL intensity I near the PL maximum by a factor of three. The same decrease in I is found when the transverse magnetic field of ~300 G is switched on. In comparison with these changes, the variation of I observed following a change of σ⁺ to σ⁻ excitation is negligibly small. Fig. 2a represents the dependence ρ(B) measured in GaAs$_{0.97}$N$_{0.03}$ layer in a transverse magnetic field B $\perp$ [001] at different intensities of the σ excitation near the PL-band maximum involving heavy holes. The dependencies are well approximated by Lorentz curves (solid lines in Fig. 2a) of the form

$$\rho(B) = \rho^* + \frac{\rho_0}{1 + (B/B_{1/2})^2},$$

where $\rho^*$ is a constant component (≈5%), $B_{1/2}$ is the half-width of the curve at half-height, $\rho_0$ is the maximum change of $\rho$ in the magnetic field. The values of $B_{1/2}$ and $\rho_0$ are strongly dependent on the pump intensity. Additional measurements show that the widths of the curves ρ(B) are equal for the positive (c-hh transition) and the negative (c-lh transition) polarization of PL measured with equal intensity of the pump light. This confirms the assumption that the photoholes are spin-unpolarized because of their fast spin relaxation and, hence, the PL polarization is caused by the polarization of electrons solely.

Fig. 2b shows the magnetic-field dependencies I(B). They can also be fitted by Lorentz curves (solid curves) with the widths coinciding with those of the Hanle curves ρ(B) taken at the same excitation intensity.

Experimental results presented in Figs. 1 and 2 can be explained in the SDR model proposed by Weisbuch and Lampel for Ga$_0.9$Al$_0.1$As solid solutions and applied in Refs. [9] while analyzing the recombination processes in GaAs crystals GaAs/AlGaAs multiple quantum-well structures. We use this model and assume that each deep center can contain either one electron with uncompensated spin ±1/2 or two electrons in the singlet state with the zero total spin. Under normal incidence of the circularly polarized light in the absence of a magnetic field, the electronic spins are polarized along the excitation direction (the axis z). Let us introduce the notations $n_\pm, N_\pm$, respectively, for the concentration of the free electrons or paramagnetic centers with the component ±1/2 of the electron spin, and $N_{\uparrow\downarrow}$ for the concentration of centers with two electrons. In the SDR model under consideration the contribution of the band-to-band recombination is neglected in the balance equations and the rate of free-carrier capture by deep levels is described by $(dn_{\pm}/dt)_{\text{rec}} = -\gamma_\pm n_{\pm} N_\mp$ for electrons and $(dp/dt)_{\text{rec}} = -\gamma_\uparrow p_{\uparrow} N_{\downarrow\downarrow}$ for holes, where $p$ is the density of holes assumed to be unpolarized irrespective of the incident-light polarization. In addition to the recombination constants $\gamma_\pm$ and $\gamma_\uparrow$, the system is characterized by two times, namely, by the spin relaxation times of free and bound electrons, respectively, $\tau_s$ and $\tau_{sc}$. Apparently, at room temperature $\tau_s \ll \tau_{sc}$. As a result, the rate equations for $n_\pm$ and $N_\pm$ take the form

$$\frac{dn_\pm}{dt} = -\gamma_\pm n_\pm N_\mp - \frac{n_\pm - n_\mp}{2\tau_s} + G_\pm,$$

$$\frac{dN_\pm}{dt} = -\gamma_\pm n_\mp N_\pm - \frac{N_\pm - N_\mp}{2\tau_{sc}} + \frac{1}{2} \gamma_\uparrow p_{\uparrow} N_{\downarrow\downarrow},$$

where $G_\pm$ are the photogeneration rate of electrons with the spin ±1/2.

For a qualitative interpretation of the behavior of the PL intensity and circular polarization as functions of the incident-light polarization and the magnetic field strength, it suffices to analyze the limiting case of weak photoexcitation where $P_\text{c}$ is small and one has $\rho^* \ll 1$.

$$I \propto 1 + aP_\text{c}P, \quad \rho = b(P_\text{c} + P_\text{c}).$$

Here $P = (n_+ - n_-)/(n_+ + n_-)$ and $P_\text{c} = (N_+ - N_-)/(N_+ + N_-)$ are the degrees of spin polarization of free and bound electrons, $P_\text{i} = (G_+ - G_-)/(G_+ + G_-)$ is the spin-polarization degree of photoelectrons in the moment of generation, and a, b are positive coefficients. Since the linearly polarized excitation gives rise to no optical orientation of electron spins, the ratio $I(\text{circ})/I(\text{lin})$ of PL intensities under circularly and linearly polarized pumping is given by $(1 + aP_\text{c}P)$, where values of $P_\text{c}, P$ refer to circularly polarized excitation. Note that the product $P_\text{i}P$ is positive and independent of the sign of the incident circular polarization. Therefore, $I(\text{circ}) > I(\text{lin})$.

In a transverse magnetic field, $B \perp z$, so that
The increasing range of $J$.

Here we show, in the system under study, in spite of the short spin-relaxation time $\tau_s$, there is also a long time of evolution of free-electron spins. For this purpose we reduced the rate equations for $n_\pm$ and $N_\pm$ to the following equations for the polarization degrees:

$$\frac{dP_+}{dt} = -\frac{P_+}{\tau_s} + \frac{P_+}{\tau_0}(1 - P_+^2) + \frac{G}{n}(P_+ - P_-),$$

$$\frac{dP_-}{dt} = -\frac{P_-}{\tau_0} + \frac{n}{N_0}P_+(1 - P_-^2),$$

where $G = G_+ + G_-$ is the total generation rate, and $\tau_0 = (2/\gamma_c N)$ is the capture time of conduction-band electrons in the absence of SDR. The second term in the right-hand side of Eq. (4) is related to SDR and plays the role of spin-generation rate. By using Eq. (4) one can readily show that, under abrupt cutting off the steady-state optical excitation ($G = 0$), the polarization time decay $P(t)$ comprises both fast and slow components: the first one decays within the time $\sim \tau_s$, whereas the second contribution can be approximated by $P(t) \approx (\tau_s/\tau_0)P_+(t)$.

The proximity of the maximum value of PL polarization ($\sim 35\%$) in Fig. 2a to its limiting value of $50\%$ indicates a long-term spin memory of conduction electrons. As shown above, the spin memory of the nonlinearly coupled spin subsystems of free and bound electrons is controlled by the long spin lifetime $T_{sc}$ of bound electrons. The latter can be easily determined from the Hanle effect as $T_{sc} = h/(g_c|\mu_B|B_{1/2})$, so that the longer $T_{sc}$ corresponds to the smaller $B_{1/2}$. The smallest half-width found from Fig. 2a is $B_{1/2}^\text{min} = (91 \pm 5)$ G. Taking into account that $\tau_{sc}^{-1} < T_{sc}^{-1}$, we obtain a lower estimate for the spin relaxation time multiplied by the $g$-factor: $g_cT_{sc} > g_cT_{sc}^\text{min} = (1.3 \pm 0.2)$ ns. The magnitude of $g_c$ in GaAsN is unknown (the available study of the electron $g$-factor in nitrogen-containing GaAs-based alloys is devoted to measurements of $g$ in GaInAsN). In a special experiment with oblique incidence of light onto the sample, when the PL is measured in the backscattering geometry at an angle to the pump beam, and the magnetic field is normal to the directions of excitation and observation, we found that $g_c > 0$. Similarly, the positive sign of $g_c$ was found in GaAsN films with the 2.7 and 3.4% nitrogen content. The sign of $g_c$ allows us to make a conclusion that its value is close to the $g$-factor of a free electron in vacuum, i.e., $g_c \approx 2$. It follows then that the bound-electron spin relaxation time $\tau_{sc}$ exceeds 0.6 ns.

In conclusion, the strong SDR has been observed in GaAsN alloys at room temperature. Giant electron spin lifetime and high polarization have been found under optical pumping conditions. Therefore, the nitrogen-containing alloys GaAsN can be considered as a promising material for the development of spintronic devices. The sensitivity of the PL circular polarization and the Hanle effect half-width to the pump intensity has been
firstly observed in a semiconductor of intrinsic conductivity type. A simple model of SDR has been applied to explain the observed dependencies of the electron lifetime, the electron spin lifetime and the degree of electron spin orientation on the pump intensity. It has been shown that, in spite of the very short spin relaxation time of free electrons, the behavior of the coupled system of spin-polarized free and bound electrons is controlled by the long spin relaxation time of bound electrons that amounts 1 ns. Using the Hanle effect, we have determined the positive sign of $g$-factor of bound electrons which are responsible for the observed SDR.

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