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TRANSIENT PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE IN InP:Cu

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Nonequilibrium photoexcited carrier dynamics in InP:Cu was investigated by two experimental techniques: the time-resolved photoluminescence up-conversion and the transient photoconductivity measurement. Both measurements show that doping with copper significantly modifies the photoexcited carrier relaxation in indium phosphide. There are several strong indications that this effect originates from the carrier trapping at metallic precipitates.

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Semi-insulating A_3B_5 semiconductors have numerous important applications as substrates for integrated circuits, microwave and optoelectronic devices. Usually, such materials are obtained by utilizing deep, near-midgap levels compensating shallow impurities. It has been proposed [1] that semi-insulating A_3B_5 materials can be created also by introduction of metallic precipitates into the semiconductor, at sufficiently large densities. Originally proposed for explaining unique properties of well-known GaAs layers grown by a low-temperature molecular-beam epitaxy (LT GaAs) the precipitate model is still far from being commonly accepted for that material. In contrary, the latest investigations indicate that the high resistivity and ultrashort carrier lifetimes in LT GaAs can be better explained by the presence of deep, excess-arsenic-related defects [2], a model alternative to the precipitate model. However, it has been observed recently [3–5] that metallic inclusions are responsible for semi-insulating behavior in another A_3B_5 material — Cu-diffused InP.

The samples studied were prepared using as-grown nominally undoped, n-type ($5 \times 10^{15}/\text{cm}^3$) InP wafers. Cu was evaporated on both sides of the samples, diffused in clean quartz ampoules and sealed. After diffusion, the samples were rapidly quenched by dropping the ampoules into liquid nitrogen. Any residual Cu was removed from the samples surfaces by a mechanical polishing followed by an etching in a bromine and methanol solution. Diffusion temperatures used were in the range from 575 to 900°C. This produced introduced Cu densities ranging from 2×10^{17} to $3 \times 10^{17}/\text{cm}^3$. After the quenching, Cu forms small precipitates with average diameters of 5 nm [4]. Estimated concentrations of the precipitates in investigated samples ranged from 1×10^{14} to $2 \times 10^{15}/\text{cm}^3$.

Nonequilibrium carrier dynamics in InP:Cu was studied by time-resolved photoluminescence (PL) and photoconductivity (PC) experiments. In a time-resolved PL measurement, a self-mode-locking Ti:sapphire laser with a central wavelength of 770 nm (photon energies around 1.61 eV), pulse duration of 100 fs, and pulse repetition frequency of 80 MHz was used. Ti:sapphire laser pulses were used both for sample excitation and sum-frequency generation. Temporal resolution of this measurement, as it was demonstrated previously [6], was about 100 fs. Average excitation intensities ranging from 10 to 100 mW were used, which corresponded to the excited carrier densities of the order of 2×10^{17}–$2 \times 10^{18}/\text{cm}^3$.

Transient PC measurements were performed by using a passively-mode-locked Nd^{3+}:$YAlO_3$ laser (pulse duration of 10 ps, pulse repetition rate of 10 Hz) for sample's excitation. Both the first ($\lambda = 1.06\ \mu$m) and the second ($\lambda = 0.53\ \mu$m) harmonics pulses were used. PC dynamics was measured by monitoring the photocurrent pulses with a high-speed oscilloscope (temporal resolution of 0.5 ns). Fast initial PC decay component was additionally studied in a nonlinear photoconductivity autocorrelation type experiment [7]. All measurements were performed at room temperature.

The effect of copper doping on the PL dynamics in InP is demonstrated in Fig. 1a. Two transients presented in this figure correspond to the reference, undoped sample and to the sample, which was diffused with Cu at 900°C and then rapidly quenched to a low temperature. PL decay curves are measured at the radiation wavelength of 930 nm corresponding to the near-band gap photon energy of 1.33 eV. Relaxation of the PL signal in InP becomes much faster after Cu diffusion, it can be best approximated by a double-exponential function. The dependencies of the characteristic decay time constants on the Cu diffusion temperature shows that a second, faster PL decay component becomes evident at the diffusion temperatures greater than 625°C when, according to previous observations [4], metal precipitates start to nucleate.

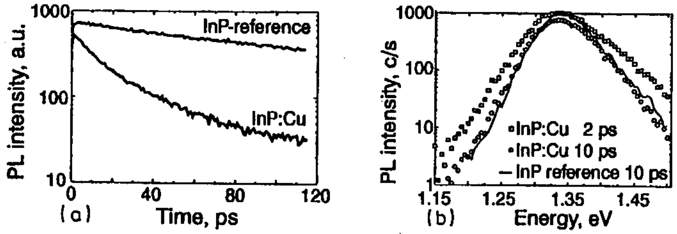

Fig. 1. Time-resolved photoluminescence up-conversion measurement by using Ti:sapphire laser: (a) PL decay at the band edge, (b) PL spectra at different times after the photoexcitation.

PL signal in InP:Cu sample decays even faster when it is monitored at photon energies smaller than the energy band gap of InP. Characteristic decay time of the PL decay, which again becomes single-exponential at the sub-band gap energies, is smaller than 3 ps for photon energies of 1.19 eV. This effect is illustrated in Fig. 1b where PL spectra of an InP/Cu sample measured at two different times after the photoexcitation are presented. PL sample of the reference, undoped with Cu sample measured at 10 ps after the excitation is also shown for comparison. PL spectra of both samples are similar at longer times after excitation, however the sub-band gap PL in InP:Cu measured immediately after photoexcitation is by almost an order of magnitude more intense than in the reference InP.

Figure 2a presents a photocurrent transient measured on a sample made from InP:Cu under a pulsed 1.06 μm excitation. Characteristic time of the PC decay (1.1 ns) is much shorter than the time constants obtained from the PL experiments. Moreover, even slower decaying photocurrent tails, which became more pronounced as the excitation level increased, were observed. Similar transients were observed also when the sample was excited by a second harmonics radiation.

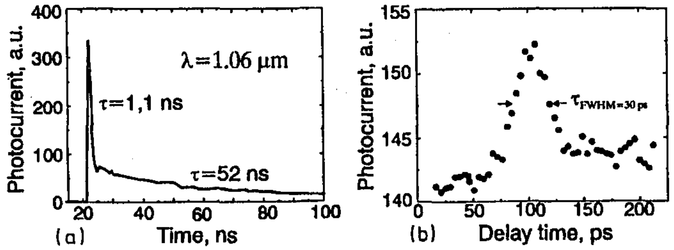

Fig. 2. Transient photoconductivity measurement by using pulsed illumination by mode-locked Nd^{3+}:$YAlO_3$ laser: (a) PC decay, (b) PC autocorrelation.

Temporal resolution of the transient photocurrent measurement was too low to observe PC changes on a picosecond time scale, therefore an additional PC autocorrelation experiment was performed. The results of this experiment are presented in Fig. 2b. PC autocorrelation trace has a 30 ps FWHM peak, which, after deconvolution with the laser pulse duration, gives a value of 20 ps corresponding to a faster PL decay constant in InP:Cu. It has to be noted that only the PC autocorrelation traces measured with 1.06 μm excitation had exhibited such picosecond peaks; no peaks were detected by 0.53 μm excitation.

Both the dynamical PL and the dynamical PC measurements show that doping with copper significantly modifies the photoexcited carrier relaxation in indium phosphide. There are several strong indications that this effect originates from the carrier trapping at metallic precipitates. Firstly, the appearance of a fast PL decay component correlates well with the Cu diffusion temperature at which the precipitates start nucleating. Secondly, the enhanced sub-band gap PL and its ultrafast decay times can also be best understood by including into explanation the presence of strong internal fields caused by electrically charged metallic precipitates in an InP:Cu crystal.

The effect of precipitate recharging on the PC dynamics can be evidenced by analyzing the origin of the peak on the nonlinear PC autocorrelation trace. Most probably, the cause of that peak is the nonlinearity of the IR, sub-band gap absorption due to the dynamical screening of the built-in fields in space-charge regions surrounding the precipitates and the quenching of Franz–Keldysh type electron transitions. When two optical pulses excite the sample simultaneously their absorption will be more intense than in the case when the carriers generated by an earlier arriving pulse screen the precipitate field and reduce the absorption of the second optical pulse. The precipitate recharging time estimated from that experiment ($\approx$ 20 ps) correlates with a corresponding characteristic time found from the PL measurements.

In conclusion, carrier dynamics in InP:Cu crystals was investigated by transient PL and PC measurements. The observed reduction of the nonequilibrium carrier trapping times as well as other features were attributed to the effects of the built-in electrical fields in the space-charge regions around metallic precipitates.

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