Persistent photoconductivity in Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$

J. Z. Li, J. Y. Lin, and H. X. Jiang

Department of Physics, Kansas State University, Manhattan, Kansas 66506-2601

J. F. Geisz and Sarah R. Kurtz

National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

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Electrical properties of unintentionally doped $p$-type Ga$_{0.95}$In$_{0.05}$N$_{0.013}$As$_{0.987}$ quaternary alloys grown by metal–organic vapor-phase epitaxy have been investigated by Hall-effect and photoconductivity measurements. Persistent photoconductivity (PPC) has been observed in this material at temperatures $T<320$ K. The PPC buildup and decay kinetics have been systematically measured at different temperatures and photoexcitation energies and formulated in the context of lattice-relaxed deep levels (or AX-like centers). The parameters which characterize the AX centers in GaInNAs, namely, the thermal and optical ionization energies, hole capture barrier, and the Stokes shift, have been determined. Our results indicate that AX-like deep levels strongly influence the electronic properties of the GaInNAs quaternary system. © 1999 American Institute of Physics.

Recently, the quaternary Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy system has attracted a great deal of attention due to its potential applications in next-generation ultra-high-efficiency multijunction solar cells as well as in optoelectronic devices for optical communications. It has been demonstrated that this quaternary alloy system can be grown lattice matched to GaAs substrates and its band-gap energy can be tailored to around 1.0 eV by incorporating only a few percent of N concentration under nonequilibrium growth conditions. The 1.0 eV Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ alloy system appears to be an ideal candidate material for the third junction in multijunction solar cells. Recently, a Ga$_{1-x}$In$_x$N$_y$As$_{1-y}$ solar cell with an internal quantum efficiency (IQE) greater than 70% has been achieved. However, the device performance is still rigidly limited partly due to the presence of defects in GaInNAs, which may result in low IQE and small minority-carrier diffusion lengths. Thus, the impurity properties in this quaternary system have to be studied thoroughly before we can take full advantage of this class of materials.

In this letter, we report the observation of a persistent photoconductivity (PPC) effect in GaInNAs materials grown on GaAs substrates. At low temperatures, the conductivity of the sample was observed to increase by more than one order of magnitude after light exposure and the photoenhanced conductivity persisted for a very long period of time after the termination of photoexcitation. The acceptor binding energy, hole capture barrier, and optical ionization energy have been obtained by utilizing Hall-effect and photoconductivity transient measurements.

The unintentionally doped $p$-type Ga$_{0.95}$In$_{0.05}$N$_{0.013}$As$_{0.987}$ samples used for this study were grown by metal–organic vapor-phase epitaxy (MOVPE) using dimethylhydrazine (DMH) as the nitrogen source. The growth procedure was similar to that reported elsewhere. Specifically, a growth temperature of 650 °C, growth rate of 7 μm/h, arsenic pressure of 0.2 Torr, and DMH/V ratio of 0.99 were used. The nominally 1 μm GaInNAs film was deposited onto a Cr-doped GaAs substrate. Ohmic contacts were made by annealing In/Zn dots onto the corners of the samples. For photoconductivity measurements, a 1.5 V bias was supplied to the sample, a Ne lamp was used as an excitation source, and an electrometer was used to monitor the current. The light intensity and buildup time span are fixed for all sample temperatures. To ensure that each set of data obtained under different temperatures has the same initial conditions, the system was always heated up to 330 K and then cooled down in darkness to the desired measurement temperatures and a 30 min waiting time was generally required before data acquisition. A halogen lamp, together with a monochromator and an infrared filter, was used as an excitation light source in the 0.75–2.5 μm wavelength region for the optical ionization energy $E_{opt}$ measurement.

Figure 1 shows the free-hole concentration $p$ as a function of reciprocal temperature obtained in darkness in the temperature range from 10 to 450 K. From the appearance of the Hall data, we can clearly see that different slopes are present in the $\ln(p)$ vs $1/T$ plot, which indicates that more than one acceptor state may be involved in the conduction process. Furthermore, alloy scattering is probably very important in this quaternary material, which can lead to a hopping conduction in the low-temperature region. However, as demonstrated in a previous work of $n$-type 6H–SiC materials in which several donor levels associated with different lattice sites are known to be involved, the average impurity thermal ionization energy ($E_a$) can be estimated from the slope of the $\ln(p)$ vs $1/T$ plot in the high-temperature region, which is about 67 meV. To be shown later, this value is much smaller than the optical ionization energy ($E_{opt}$) of about 700 meV. The inset shows the hole mobility $\mu_p$ as a function of temperature. Scattering mechanisms in different temperature regions in this material remain to be studied. However, the variation of $\mu_p$ with temperature indicates that the change in...
the conductivity with temperature is predominantly caused by the change in the free-hole concentration.

The GaInNAs films used here exhibit a pronounced PPC effect. A typical example of the PPC behavior is illustrated in inset (a) of Fig. 2, which shows that the conductivity at 150 K increases by more than one order of magnitude after exposure to light and the light-enhanced conductivity persists for a very long period of time after light illumination is terminated. Figure 2 shows the normalized PPC decay curves obtained at three representative temperatures, in which the PPC decay curves have been normalized to unity at \( t = 0 \) (the moment the illumination is terminated) according to \( I_{PPC}(t) = [I(t) - I_d]/[I(0) - I_d] \). Here, \( I(0) \) is defined as the current level immediately after the termination of the excitation source, \( I(t) \) the current at the decay time \( t \), and \( I_d \) the initial dark current level. One can see that the PPC relaxation time becomes very long below 175 K. The PPC level is still about 75% of its initial value after 1000 s of decay at 175 K. However, as the sample temperature was increased to above 320 K, no PPC effect was observed.

The PPC decay behavior in the investigated temperature region (50–320 K) is very well described by a stretched-exponential function, which is frequently used to describe the PPC relaxation in a wide class of III–V and II–VI semiconductors. The time-dependent normalized PPC decay \( I_{PPC}(t) \) can be written as

\[
I_{PPC}(t) = \exp[-(t/\tau)^\beta],
\]

where \( \tau \) is the characteristic decay time constant and \( \beta (0 < \beta < 1) \) the decay exponent.

The variation of the decay time constant \( \tau \) with temperature has been determined by fitting PPC decay data with Eq. (1) and the results are shown in inset (b) of Fig. 2. One of the noticeable features observed in inset (b) of Fig. 2 is that the Arrhenius plot of the PPC decay time constant \( (\ln \tau vs 1/T) \) shows two distinct temperature regions. At temperatures \( T > 220 \) K, \( \tau \) decreases rapidly with temperature following an activated behavior. However, \( \tau \) is only weakly dependent on temperature at \( T < 220 \) K. The decay exponent \( \beta \) increases linearly with \( T \) at \( T > 200 \) K and is also nearly temperature independent at \( T < 200 \) K. Detailed studies show that the PPC decay kinetics observed here are similar to those of DX centers in Al\(_0\)Ga\(_{1-x}\)As alloys and GaN.

It is widely accepted that deep-level traps (DX or AX centers), which undergo a large lattice relaxation upon photoexcitation, are responsible for the phenomenon of PPC in Al\(_0\)Ga\(_{1-x}\)As. According to this model, the PPC decay is caused by the process of thermal activation of carriers over a capture barrier \( E_c \) in the high-temperature region and is due to electron tunneling via multiphonon emission in the configurational space in the low-temperature region. Consequently, two distinctive temperature-dependent capture characteristics can be observed. Results shown in Fig. 2 indicate that there is an energy barrier of about 0.57 eV which prevents free-hole capture by ionized AX-like centers.

Another important feature that characterizes the AX-like centers is the existence of a Stokes shift, which is the lattice relaxation energy associated with hole capture by an AX center. The optical ionization energy has been measured for DX centers in AlGaAs materials, in which a Stokes shift of about 1.0 eV has been obtained. In this work, we have employed the PPC buildup transient measurements to determine the optical ionization energy \( E_{opt} \) of AX-like centers in GaInNAs. Figure 3 shows the room-temperature PPC buildup and decay transients measured at different excitation photon energies \( h\nu \). When the dark current levels are subtracted out, the PPC buildup transients can be well described by

\[
I_{PPC}(t) = I_{max} [1 - \exp(-t/\tau_i)],
\]

where \( I_{max} \) is the saturation level and \( \tau_i \) the buildup characteristic time constant, both of which are correlated with the optical cross section. Figure 4 shows the relative optical...
cross-section $\sigma_{\text{opt}} \propto \left( \frac{I_{\text{max}}}{\tau_{\phi}} \right)$, with $\phi$ being the relative photon flux at different excitation energies, as a function of $h\nu$. $E_{\text{opt}}$ can be obtained by fitting the relative optical cross-section to

$$\sigma_{\text{opt}} \propto (h\nu - E_{\text{opt}})^{1.5} (h\nu)^3.$$  

The least-squares fitting result to the data (solid lines) in Fig. 4 yields $E_{\text{opt}} = 0.70$ eV. This gives a Stokes shift of about 0.64 eV ($= E_{\text{Stokes}} = E_{\text{opt}} - E_a$). Such a large energy, which is one of the common features of lattice relaxation associated with impurities, provides an additional evidence that AX-like centers are the primary cause of PPC in GaInNAs. Residual carbon acceptors may be a candidate for the AX-like centers, but our results cannot provide insight regarding this or the number of holes released by the AX-like centers under illumination. However, based on these results, the band structure in the configurational coordinates, which illustrates the energy parameters of the AX-like centers, can be constructed and is schematically shown as an inset of Fig. 4.

In summary, a PPC effect has been observed and studied in GaInNAs materials. The decay of PPC is found to follow a stretched-exponential function. It is believed that the AX-like centers are predominantly responsible for the PPC effect in GaInNAs. The energy parameters which characterize the AX-like centers have been measured, while their origin remains to be investigated.

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