

Transport properties of nitrogen doped p -gallium selenide single crystals

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Nitrogen doped gallium selenide single crystals are studied through Hall effect and photoluminescence measurements in the temperature ranges from 150 to 700 K and from 30 to 45 K, respectively. The doping effect of nitrogen is established and room temperature resistivities as low as 20 Ω cm are measured. The temperature dependence of the hole concentration can be explained through a single acceptor-single donor model, the acceptor ionization energy being 210 meV, with a very low compensation rate. The high quality of nitrogen doped GaSe single crystals is confirmed by photoluminescence spectra exhibiting only exciton related peaks. Two phonon scattering mechanisms must be considered in order to give quantitative account of the temperature dependence of the hole mobility: scattering by 16.7 meV A_1' homopolar optical phonons with a hole-phonon coupling constant $g^2=0.115$ and scattering by 31.5 meV LO polar phonon with a hole Fröhlich constant $\alpha_{hL}=0.741$. © 1996 American Institute of Physics. [S0021-8979(96)08101-3]

I. INTRODUCTION

Gallium selenide (GaSe) has been widely investigated in the last years because of its outstanding nonlinear optical properties.¹⁻⁸ The possibility of preparing GaSe high-quality thin films through the so-called van der Waals epitaxy⁹⁻¹² has lead to a renewed interest because of the potential optoelectronic applications. The problem of doping, that was early investigated without drawing definitive conclusions,¹³⁻¹⁸ has been recently attacked by other groups that have specially studied the role of group II impurities as acceptors in GaSe.¹⁹⁻²³ Attempts to get low resistivity n -type GaSe have been up to now unsuccessful.²⁴

Room temperature (RT) hole concentrations of the order of 10^{16} cm⁻³ have been reported by doping with Zn²² and Cd.²¹ Activation energies for hole concentration are of the order of 300 meV for Zn,²² Cd,²¹ or Mn²³ doped GaSe.

Nitrogen (N) has been successfully used as an acceptor in II-VI semiconductors like ZnSe,²⁵⁻²⁹ which suggests that it can play the same role in III-VI layered compounds. In this article we report on transport properties and photoluminescence (PL) of N-doped GaSe. We also discuss the scattering mechanisms involved in the temperature dependence of the hole mobility in GaSe.

II. EXPERIMENT

The GaSe crystals used in this study were grown by the Bridgman method from a stoichiometric melt of GaSe. Nitrogen was introduced as GaN compound in a quantity to give a 0.1 (ingot N1) and 0.5 (ingot N2) at. % of nitrogen in the melt. The growth system was technically improved by installing a pulling head that prevents mechanical vibrations and allows for ampoule rotation, which contributes to the homogeneity of the liquid phase. Computer control of the temperature gradient and ampoule displacement also contrib-

ute to the stability and reproducibility of the growth process. All these improvements result in high-quality monocrystalline ingots.

Square samples with faces perpendicular to the c axis were prepared from the ingots by cleaving and cutting with a razor blade. The interference fringe pattern in the infrared transmission spectrum was used to measure the thickness of the slabs, that ranged from 10 to 40 μ m. Typical dimensions of the samples were 4×4 mm². Ohmic contacts for Hall effect (HE) measurements were made by soldering with high-purity indium in the van der Pauw configuration.³⁰

Low temperature HE and PL measurements were carried out in a Helium closed cycle Leybold Heraeus cryogenic system. For HE measurements between 300 and 700 K the sample was heated in vacuum in a system implemented at the laboratory. The current flows along the layer plane and the magnetic field (0.6 T) was applied perpendicular to it. The linearity of the Hall and ohmic voltages on the injected current was checked out at each temperature. PL measurements at low temperature (from 30 to 45 K) were carried out by exciting with the 514 nm line of an air cooled Ar⁺ laser 100 mW in intensity. The PL signal was analyzed with a H25 Jobin-Yvon monochromator and synchronously detected with a Si photodiode and a lock-in amplifier.

III. RESULTS

Table I gives the typical values of the RT resistivity and hole concentration of samples from N1 and N2 ingots compared to those of not purposely doped GaSe grown in the same conditions. The p -doping effect of N clearly appears in those results. Figure 1 shows the temperature dependence of resistivity for samples from ingots N1 and N2. The weak temperature dependence of resistivity in samples from ingot N2 above 300 K clearly indicates an extrinsic behavior that is confirmed by HE results.

TABLE I. RT resistivity and hole concentration for N-doped GaSe samples from N1, N2 ingots and not purposely doped GaSe grown in the same conditions (N0 ingot).

Ingot	Doping agent	Concent. (% at. dopant)	$\rho_{300\text{ K}}$ ($\Omega\text{ cm}$)	$p_{300\text{ K}}$ (cm^{-3})
N0			10^6	10^{11}
N1	N	0.1	10^4	10^{13}
N2	N	0.5	20	4×10^{15}

Figure 2 shows the temperature dependence of the hole concentration for several slabs of N-doped GaSe from ingots N1 and N2 as determined through

$$p = \frac{1}{|q|R_H}, \quad (1)$$

where q is the electron charge and R_H is the Hall coefficient. The Hall factor has been assumed to be 1. This assumption is in agreement with HE measurements in other layered semiconductors.^{31,32} From Fig. 2 we see that the carrier concentration reaches a nearly constant value of $1.5 \times 10^{16} \text{ cm}^{-3}$ at temperatures higher than 400 K and decreases by two orders of magnitude at low temperature exhibiting an activated behavior over the temperature range from 150 to 300 K. Fitting curves are also included and fitting parameters are shown in Table II. The model used for this fitting process will be discussed in the next section.

Figure 3 shows the temperature dependence of the hole mobility for several samples from the N2 ingot. The temperature dependence of the hole mobility changes from $T^{-1.8}$ in the range from 150 to 300 K to $T^{-1.05}$ in the range from

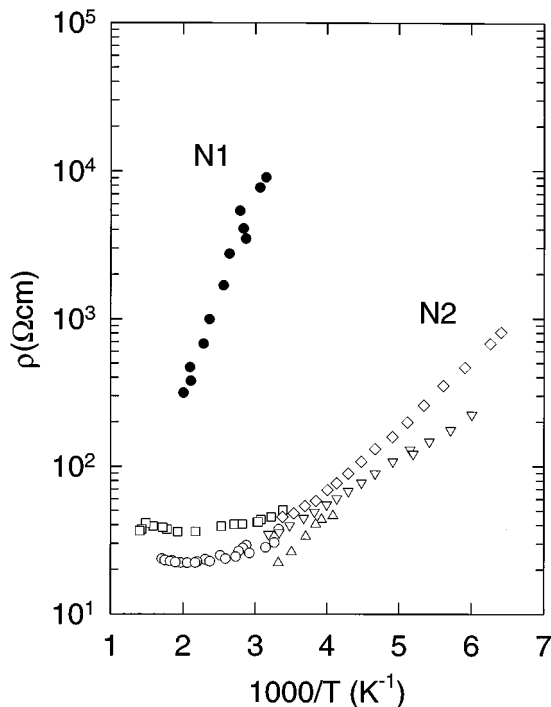


FIG. 1. The temperature dependence of the resistivity of N-doped GaSe. Experimental points obtained from slabs from N1 (●) and N2 (○, △, ▽, □) ingots.

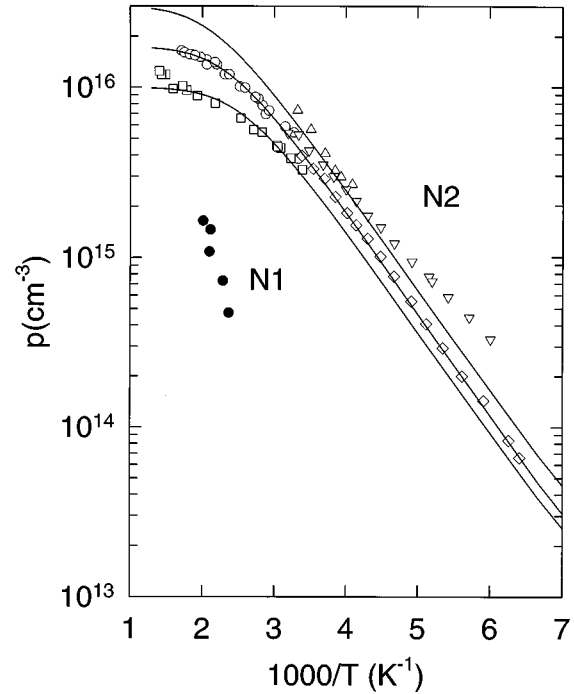


FIG. 2. The temperature dependence of the hole concentration of N-doped GaSe. Experimental points obtained from slabs from N1 (●) and N2 (○, △, ▽, □) ingots. Solid lines correspond to fitting curves with $E_a=208$, 210, and 212 meV and with $N_a=2.2 \times 10^{16}$, 1.7×10^{16} , and 10^{16} cm^{-3} for the higher, the medium, and the lower curves, respectively.

400 to 700 K. This dependence suggests that phonon scattering mechanisms predominate even down to 100 K, despite the acceptor impurities. This reflects the high crystalline quality of samples. Fitting curves are also included. The model used for this fitting process will be discussed in the next section.

Figure 4 shows PL measurements at low temperature (from 30 to 45 K). The PL spectra only exhibit peaks appearing in GaSe samples prepared in the same way without any added impurity.^{21,22} Two peaks at 2.098 and 2.075 eV are resolved. The inset of Fig. 4 is the Arrhenius plot of the intensity of those PL peaks, that yields an activation energy of 50 meV for the thermal quenching of the peaks.

IV. DISCUSSION

A. Analysis of doping effects

From resistivity and hole concentration at room temperature (Table I) the doping effect of nitrogen in GaSe seems to be clearly established. The behavior of resistivity and carrier concentration (Figs. 1–2) is extrinsic and the exhaustion region is attained at 500 K. Therefore, we can analyze the temperature dependence of the carrier concentration through a single acceptor-single donor model for partially compensated p -type semiconductors³³ ruled by the equation

$$\frac{p(p+N_d)}{N_a-N_d-p} = \frac{N_v}{\beta} \exp\left(\frac{-E_a}{k_B T}\right), \quad (2)$$

where p is the hole concentration, T is the absolute temperature, N_d is the donor-impurity concentration, N_a is the

TABLE II. Summary of the transport parameters and ionization energies of N-doped GaSe, compared to those of GaSe with other doping agents found in the literature.

Doping agent	Doping concent. (at. %)	300 K							Ref.
		ρ (Ω cm)	p (cm^{-3})	μ ($\text{cm}^2/\text{V s}$)	N_a (cm^{-3})	N_d/N_a	p/N_a (%)	E_a (meV)	
N undoped	0.5	20	4×10^{15}	37	1.7×10^{16}	2×10^{-4}	24	210	this work
Zn	10	5×10^2	5×10^{15}	35	8.4×10^{16}	0.95	6	40	14
Zn	0.5		4×10^{14}	31	$\sim 10^{17}$		0.4	180	24
Mn	1		8×10^{15}		1.4×10^{17}	8×10^{-5}	6	310	22
Cd	1		2×10^{13}		3.1×10^{15}	0.29	0.6	340	23
			1×10^{16}		4.1×10^{17}	2×10^{-5}	2	270	21

acceptor-impurity concentration, E_a is the ionization energy of the acceptor-level, k_B is the Boltzmann constant, β is the degeneracy factor, which is taken as $\beta=2$ in these calculations, and N_V is the density of states of the valence band that can be written in the usual three-dimensional case as a function of the density of state effective mass in the valence band $m_v^* = (m_{h\perp}^* m_{h\parallel}^*)^{1/3}$ as

$$N_V = 4.83 \times 10^{15} T^{3/2} (m_v^*/m_0)^{3/2} \text{ cm}^{-3},$$

where m_0 , $m_{h\perp}^*$, and $m_{h\parallel}^*$ are the free electron mass, the perpendicular and parallel effective hole mass respectively. Solving (2), we can write

$$p = \frac{N_d}{2} \left\{ -1 - \frac{N_V}{2N_d} \exp\left(\frac{-E_a}{K_B T}\right) + \sqrt{1 + \frac{N_V}{N_d} \exp\left(\frac{-E_a}{K_B T}\right) \left[\frac{N_V}{4N_d} \exp\left(\frac{-E_a}{K_B T}\right) + 2\frac{N_a}{N_d} - 1 \right]} \right\}. \quad (3)$$

We have fitted Eq. (3) to the measured hole concentration (Fig. 2) taking $m_{h\perp}^* = 0.8m_0$ and $m_{h\parallel}^* = 0.2m_0$ ^{34,35} which implies a value of $m_v^* = 0.5m_0$. We have obtained a good agreement with experimental results (solid lines in Fig. 2). The fitting parameters are shown in Table II, in average value. In Table II we have compared the transport parameters and ionization energies of N-doped GaSe to those of GaSe with other doping agents reported in the literature. The proportion

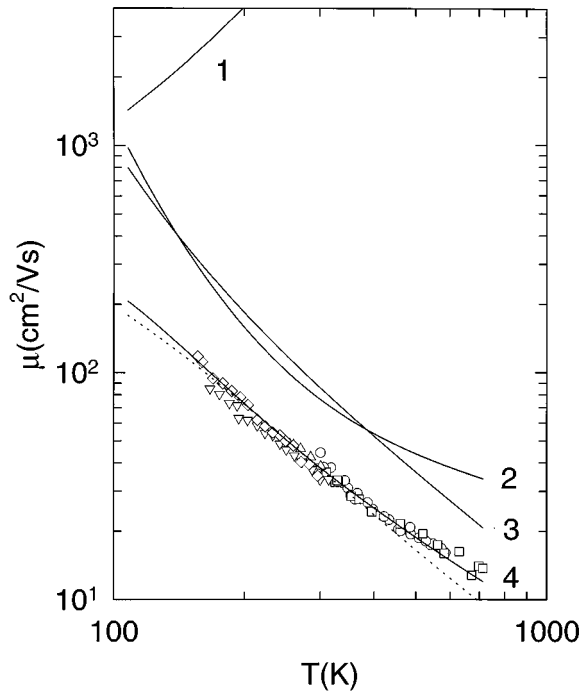


FIG. 3. The temperature dependence of the hole mobility of N-doped GaSe. Experimental points obtained from samples from N2 ingot ($\circ, \triangle, \nabla, \square$). The dotted curve is the calculated drift mobility including only ionized impurities and homopolar phonon scattering with $g^2=0.25$. Curves 1, 2, and 3 are the contributions to the hole mobility of ionized impurities, homopolar phonon scattering ($g^2=0.115$) and LO polar phonon scattering ($\alpha_{h\perp}=0.741$), respectively. Curve 4 is the calculated hole mobility when the three scattering mechanisms are included.

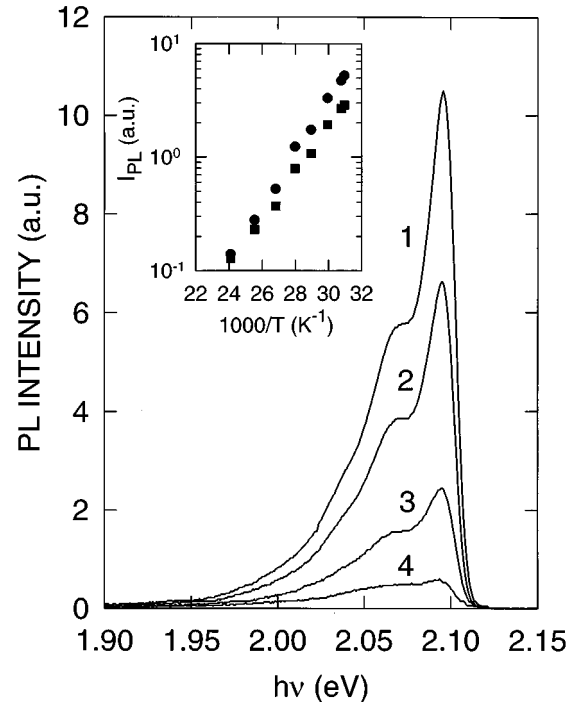


FIG. 4. The PL spectra of N-doped GaSe for samples from N2 ingot: (1) 32 K, (2) 33 K, (3) 36 K, and (4) 39 K. Inset: Arrhenius plot of the intensity of the PL peaks.

of the hole concentration with respect to the acceptor concentration is the highest one in N-doped GaSe. The RT hole mobility is also among the highest ones.

Let us discuss the PL results. The low temperature PL spectrum of high-purity GaSe is characterized by four peaks at 2.098, 2.075, 2.035, and 1.988 eV, labeled by Capozzi¹⁶ as A, B, C, D. This author assigned A and C to direct and indirect free exciton recombination, respectively, with B and D to the recombination of direct and indirect excitons bound to native impurity centers. He also points out that the absolute minimum of the conduction band occurs at the *M* point of the hexagonal Brillouin zone, a few tens of meV below the relative minimum at the Γ point, which makes the direct exciton resonant with the states of the *M* minimum. Both minima can be coupled through impurity and phonon scattering, which makes PL lines in GaSe larger than in more conventional tetrahedrally bounded semiconductors.

The PL spectra of N-doped GaSe (Fig. 4) exhibit peaks A and B. Peaks C and D are unresolved in our experiment but the low energy tail corresponds to the energies given by Capozzi.¹⁶ Then, the features of the PL spectrum support the high crystalline quality of N-doped GaSe and suggest a supplementary advantage of nitrogen as doping agent in GaSe. The PL spectrum of Zn²² or Cd¹⁹ doped GaSe, with the same RT hole concentration, is dominated by strong PL bands from complex centers, indicating that a high concentration of acceptors are closely associated with native or doping induced donors. This is not the case for N-doped GaSe, which suggests a different behavior of N with respect to impurities from groups I and II. In the related compound InSe,^{31,36–38} these impurities act as acceptors when they are substituted for In, but they can act as donors when they are in an interlayer site.³⁸ The low compensation rate of N-doped GaSe and the PL spectrum seem to indicate that nitrogen does not create donor centers in GaSe. This is probably due to the high electronegativity of N, making the substitutional acceptor (N in Se site) to be the most likely configuration of N in GaSe.

A word should be said about the thermal quenching of exciton related PL peaks in our samples. The PL spectrum is quenched at relatively low temperature, with an activation energy of 50 meV. It suggests that N-doped GaSe contains nonradiative recombination centers with high capture cross-sections above 45 K. A further investigation with higher excitation intensities is needed to elucidate the role of those centers.

B. Temperature dependence of hole mobility

The temperature dependence of the hole mobility follows the trends of previously reported results.^{14,24,39} As the explored temperature range has been extended up to 700 K, we have tested the model of nonpolar optical phonon scattering proposed by Fivaz-Schmid.^{24,40} We have calculated the hole mobility with the following assumptions:

- (i) The phonon involved in the scattering is the 16.7 meV A'_1 mode.³⁹
- (ii) The value of the hole-phonon coupling constant is that proposed by Schmid $g^2=0.25$.³⁹

- (iii) The ionized impurity scattering is included through the Brooks-Herring relaxation time⁴¹ in which the ionized impurity concentration has been assumed to be that obtained from the temperature dependence of the hole concentration (Table II).

The dotted line in Fig. 3 corresponds to this calculation. It fits the experimental results below 450 K. Above 450 K the calculated mobility decreases as $T^{-3/2}$, in contrast with the $T^{-1.05}$ dependence of the experimental results. This suggests that a different phonon scattering mechanism must be also taken into account.

The possible phonon scattering mechanisms that have not been considered are LA phonons and LO polar phonons. The Bardeen-Shockley model for longitudinal acoustic-phonons,⁴² with the deformation potential calculated by Schlüter⁴³ $E_{ac}=3.2$ eV and the elastic modulus of GaSe $c_{11}=1.05\times 10^{11}$ Pa,⁴⁴ leads to a hole mobility of the order of 10^3 cm²/V s at 300 K, some 30 times the actual values, which means that this scattering mechanism can be neglected.

The Fröhlich constant⁴⁵ for interaction of holes with LO phonons propagating parallel to the layers ($\hbar\omega_{LO}=31.5$ meV⁴⁶) can be calculated from data found in the literature;⁴⁷ it is $\alpha_{h\perp}=0.741$. With these values for $\hbar\omega_{LO}$ and $\alpha_{h\perp}$ we have calculated the hole drift mobility limited by LO polar phonon scattering by an iteration method^{48,49} in the whole temperature range. The result is shown in Fig. 3 (Curve 2). The RT value of the hole mobility would be 75 cm²/V s, which means that LO polar phonon scattering is an effective mechanism and cannot be neglected. Nevertheless, this mechanism alone does not give account of the experimental temperature dependence. Then, we must introduce the homopolar phonon and ionized impurity scattering mechanisms. For those mechanisms a relaxation time can be used; it is introduced in the elastic term of the scattering rates in the iteration method.⁴⁹ The coupling constant for nonpolar phonons is the only fitting parameter. Curve 4 in Fig. 3 corresponds to $g^2=0.115$ and fairly fits the experimental results.

V. CONCLUSIONS

HE and PL measurements on N-doped GaSe have been carried out. HE measurements have shown that doping with N leads to an effective reduction of resistivity and a total acceptor concentration in a significant range (10^{16} cm⁻³). The low compensation rate and the ionization energy of $E_a=210$ meV lead to a relatively high proportion of ionized acceptors at RT, yielding hole concentrations of the order of 4×10^{15} cm⁻³. These results are encouraging and suggest that resistivity can be still reduced by one order of magnitude with a higher doping concentration.

Low temperature PL spectra are ruled by excitonic recombinations. This result is coherent with the low degree of compensation revealed by transport measurements and shows that nitrogen is one of the most suitable acceptor impurities in GaSe.

The temperature dependence of the hole mobility has been explained by phonon scattering mechanisms. This fact reflects that, besides the acceptor impurities, the defect con-

centration in N-doped GaSe samples is relatively low. A re-evaluation of the relative weight of phonon scattering mechanisms leads to the conclusion that LO polar phonon scattering cannot be neglected, which results in a reduction of the coupling constant of holes to homopolar phonons, with respect to previous estimations in which the Fröhlich interaction was neglected.

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