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Phosphorus antisite defects in low-temperature InP

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We have studied low-temperature molecular-beam-epitaxy-grown InP using a variety of experimental techniques. Hall effect and far-infrared absorption under hydrostatic pressure have been employed to determine the ionization energies of two dominant donor levels at 0.11 eV above and 0.23 eV below the conduction-band Γ minimum. Measurements of photoluminescence and optically detected magnetic resonance indicate that those two levels are first and second ionization states of the phosphorus antisite double donor defect. The present results demonstrate that the antisite is a prevalent defect responsible for electrical and optical properties of the nonstochiometric, low-temperature InP.

Low-temperature (LT) growth of thin semiconductor films has recently attracted much attention.[1,2] It has been shown that lowering the growth temperature allows preparation of highly nonstoichiometric compound semiconductors. In the case of GaAs films of good structural quality with 1–2 % excess of arsenic and as much as 10^{20} cm^{-3} arsenic antisite defects can be achieved by molecular-beam epitaxy.[1] These results have stimulated efforts to understand electrical and structural properties of LT indium phosphide.[3–7] It was found that the LT InP epilayers were highly conductive and that the dominant intrinsic deep defect was present in concentrations as high as 10^{19} cm^{-3}.[6,7]

In this paper we present results of our comprehensive studies of LT InP by means of Hall effect, far-infrared absorption under high hydrostatic pressure, photoluminescence (PL), and optically detected magnetic resonance (ODMR) measurements. We determine the ionization energies of the two dominant donor levels and show that these levels are associated with the phosphorus antisite double donor defect.

We investigated InP samples grown by gas-source molecular-beam epitaxy (GS MBE) on (001) semi-insulating InP:Fe substrate. The growth technique has been described elsewhere.[6,7] Both undoped and Be-doped 1-μm-thick LT epilayers were grown at temperatures ranging from 130 °C to 500 °C. The growth parameters of the investigated samples are listed in Table I. The Hall effect measurements were done using a variable-temperature system covering the temperature range 5–300 K. The far-infrared absorption measurements were performed on samples 3, 4, 5, and 6 using a Digilab FTS 80-V spectrometer. In the high-pressure experiments sample 5 was placed in the diamond-anvil cell (DAC) with liquid nitrogen as a pressure medium. The technique for performing transmission spectroscopy in a DAC has been presented elsewhere.[8] All spectra were taken at $T=5$ K. PL measurements were done using a Janis variable-temperature cryostat. PL was excited with the 514.5-nm Ar^+ line. PL emissions from the epilayers were analyzed with an Instruments SA $\frac{1}{4}$-m monochromator and monitored by a cooled North Coast Ge detector. ODMR experiments were performed with a modified Bruker 200D ESR spectrometer.

First, we discuss how the growth temperature T_g and Be doping affect the electronic transport in the LT epi-

TABLE I. GS MBE growth parameters of the investigated InP epilayers.

Sample no.	Substrate temperature T_g (°C)	Dopant	Dopant source temperature T_D (°C)
1	500	none	
2	350	none	
3	310	none	
4	265	none	
5	200	none	
6	130	none	
7	350	Be	850
8	310	Be	860
9	310	Be	840
10	300	Be	835
11	265	Be	850
12	200	Be	850
13	130	Be	850

layers. In the case of undoped material we found that the free-electron concentration was very weakly temperature dependent even for the samples grown at high temperatures (500 °C). At low T_g below 350 °C, free carrier concentration became completely temperature independent over the entire temperature range 5–300 K. This metallike behavior indicates that the electrons form degenerate gas in the conduction band. The room-temperature electron concentration and mobility as a function of T_g are shown in Fig. 1(a). It is interesting to note that in the temperature range 265 °C to 500 °C the electron concentration dramatically increases with decreasing T_g. For samples grown at $T_g \leq 265$ °C the concentration saturates at about 4×10^{18} cm^{-3}. The rapid increase in the free-electron concentration with decreasing growth temperature indicates a temperature-dependent incorporation of native donorlike defects. In the following we will address the issues of the microscopic origin and electronic properties of these defects.

As seen in Fig. 1(a) the saturation of free-electron concentration, observed at low T_g, is accompanied by a drop in electron mobility. One possible explanation is that the mobility reduction is associated with an onset of the conduction in a narrow impurity or defect band. To clarify this point we have performed measurements of far-infrared absorption in the samples with the highest electron concentrations (samples 3,4,5,6). In the wavelength range $10<\lambda<25$ μm we observed spectra which are characteristic for free carrier absorption (FCA). This absorption originated from the LT epilayers and not from the InP substrate used as a reference sample. From the analysis of the spectral dependence of the absorption coefficient $\alpha_{FCA}(\lambda)$ it was found that α_{FCA} was proportional to $\lambda^{3.4}$. The observed wavelength dependence is very close to $\lambda^{3.5}$ predicted for α_{FCA} resulting from scattering of electrons by charged centers in a wide conduction band.[9] These results prove that the mobile electrons are located in the conduction band rather than in a narrow impurity or defect band.

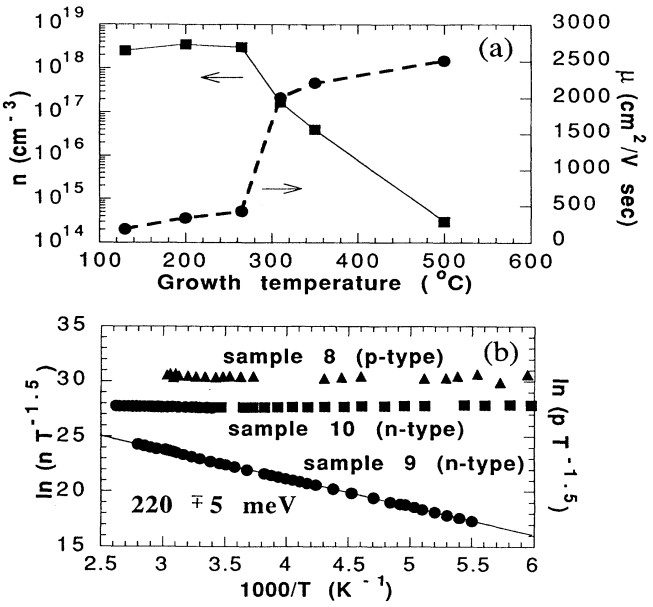

FIG. 1. Electronic transport in the LT InP: (a) room-temperature free carrier concentration n and mobility μ in undoped InP epilayers as a function of the growth temperature; (b) Arrhenius plot of the carrier concentration for the samples 8, 9, and 10. As a result of the linear fit to experimental data (solid line) activation energy 220±5 meV was obtained.

There are two possible explanations for the electronic properties of the LT epilayers—low-temperature growth results in the formation of (1) shallow hydrogeniclike donors or (2) a deep, localized donor level is resonant with the conduction band (CB) and gives rise to the high electron concentration via autoionization. In order to determine the character of the donor level, i.e., whether it is shallow, with small ionization energy, or deep, highly localized, degenerate with the CB, we have performed measurements of the free carrier absorption under high hydrostatic pressure (p). The wave function of shallow hydrogeniclike defects, localized in **k** space, is mostly built up from the states of the Γ minimum of the conduction band. Their energy levels simply follow the Γ-point energy with increasing pressure. On the other hand, the deep states, delocalized in the momentum space, are built up of the lowest conduction band averaged over the entire Brillouin zone. Thus, the pressure derivative of its energy should be the same as that of the average conduction-band energy E_{CB}, which can be evaluated using the special points scheme:[10]

$$dE_{CB}/dp=(dE_\Gamma+3\,dE_X+4\,dE_L)/8\,dp\ , \qquad (1)$$

where E_Γ, E_L, and E_X are, respectively, the energies of the Γ, L, and X CB minima with respect to the valence-band top. Using the reported pressure derivatives of the CB minima for InP [$dE_\Gamma/dp=84\pm5$ meV/GPa, $dE_X/dp=-20\pm10$ meV/GPa, and $dE_L/dp=37\pm10$ meV/GPa (Refs. 11–13)] we find $dE_{CB}/dp=22\pm6$meV/GPa. This indicates that the highly localized, deep level should approach the Γ CB minimum with a relatively high pressure coefficient of $dE_\Gamma/dp-dE_{CB}/dp=62\pm8$ meV/GPa.

In order to test these two possible origins of the free-electron concentration we measured the free carrier absorption in the highly n-type sample 5 ($n_{(p=0)}=4\times10^{18}$ cm^{-3}) at different hydrostatic pressures and the results of this experiment are presented in Fig. 2. Clearly, in the pressure range $p=0$–1.6 GPa, FCA rapidly decreases with increasing pressure and it vanishes at about $p=1.7\pm0.1$ GPa. This pressure-induced disappearance of the free electrons from the conduction band can be only explained assuming that there is a deep donor level, resonant with the conduction band at $p=0$, which via autoionization provides electrons to the conduction band. With increasing pressure the donor level moves down in energy with respect to the Γ CB minimum and captures the free electrons, leading to the change of the defect charge state as well as a decrease and subsequent disappearance of FCA at $p=1.7$ GPa. The lowest carrier concentration we can measure with the Fourier transform infrared– (FTIR) DAC setup is about 1×10^{17} cm^{-3}. Consequently, the calculated transition pressure p_c at which the deep level enters the energy gap is found to be $p_c=1.8\pm0.1$ GPa. Applying Eq. (1), we estimate the thermal ionization energy of the donor level at ambient

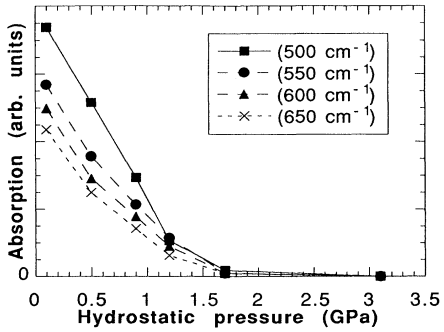

FIG. 2. Far-infrared optical absorption of sample 5 for different photon energies as a function of the hydrostatic pressure at $T=5$ K.

pressure to be 0.11 ± 0.02 eV above the bottom of the conduction band.

It has to be stressed that this energy agrees very well with the Fermi level position ($E_F=E_\Gamma+0.12$ eV) derived from the upper saturation limit of the free-electron concentration $n=4\times10^{18}$ cm^{-3} found for all the LT epilayers grown at $T_g\leq265$ °C and in other studies of nonstoichiometric phosphorus-rich LT InP.[4,6,7] A similar Fermi-level pinning position was observed in the surface layer of bulk material annealed under phosphorus overpressure.[14] This finding implies that the higher the deviation from InP stoichiometry, the higher the incorporation of the defects responsible for the increase of the electron concentration and transition from the nondegenerate to degenerate electronic transport. In any instance, the Fermi energy cannot be higher than the energy position of the deep level at $E_\Gamma+0.11$ eV.

Although the $E_\Gamma+0.11$ eV defect level controls electrical properties of LT InP, there is still an open question as to whether there are other levels associated with the same defect. It has been shown recently that a defect level at about $E_\Gamma-0.3$ eV exists in this material.[6,7] To verify if this defect level is also present in our samples we have studied LT InP doped with shallow Be acceptors. Based on the results of Hall effect measurements we distinguish two kinds of Be-doped samples. For the samples grown at lower temperatures $T_g\leq265$ °C (samples 11,12,13) even a heavy Be doping did not affect the n-type conduction of the epilayers and the free-electron concentration remained at 4×10^{18} cm^{-3}, i.e., the same as that observed for the undoped material. On the other hand, for growth temperatures $T_g\geq300$ °C the Be-doped samples were found to be either n-type or p-type depending on the compensation ratio and Fermi-level energy determined by the relative concentrations of Be acceptors and intrinsic donor defects. For the samples with moderate compensation ratio the free carrier concentration was very strongly temperature dependent [see Fig. 1(b)] due to the freezeout of free electrons onto a deep level lying below the bottom of the conduction band. From the slope of the Arrhenius plot $\ln(nT^{-3/2})$ versus $1/T$ [see typical results in Fig. 1(b)] we determined the thermal ionization energy of this level to be $E_\Gamma-(220\pm5)$ meV. No other deeper levels in the energy gap were detected in all the investigated samples.

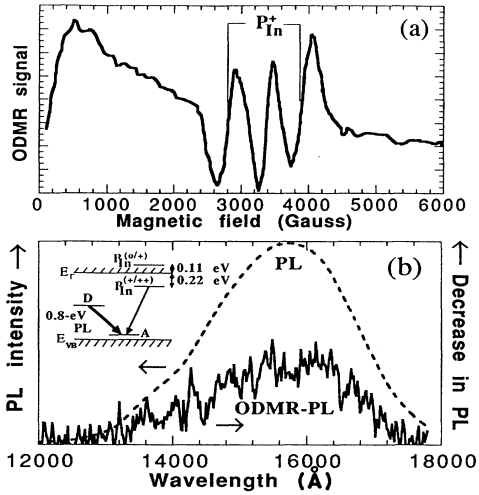

FIG. 3. (a) ODMR spectrum from sample 9 take at $T=4$ K and microwave frequency $f=9.473$ GHz. (b) PL spectrum and spectral dependence of the P_{In}^+ ODMR signal from sample 9 at $T=4$ K. On the inset the electronic structure of the P_{In} antisite and recombination processes involved are shown (see text). The microscopic identity of the donor D and acceptor A is unknown.

From the Hall effect measurements and the FTIR-DAC experiments discussed above, we have shown that there exist two deep levels; one at $E_\Gamma-0.23$ eV and another at $E_\Gamma+0.11$ eV. These levels must be related to deep defects which are preferentially formed during a low-temperature growth of nonstoichiometric epilayers. It has been speculated that under such growth conditions the properties of the material are dominated by the phosphorus antisites (P_{In});[5-7] however, there has been no experimental evidence for the presence of P_{In} in LT InP so far.

Here, we were able to unambiguously identify the presence of P_{In} antisites in LT InP by ODMR. As shown in Fig. 3(a) the ODMR spectrum is dominated at approximately $g=2$ by one doublet and one single resonant line in the middle. Variations in the relative intensities of the doublet and singlet lines observed in different samples indicates that those two features originate from different defects. The origin of the singlet is still unknown; however, the correlation between the singlet intensity with the Be doping level indicates that the corresponding defect is probably Be-related acceptor.

The angular dependence study shows that the doublet is isotropic, arising from an unpaired electronic spin ($S=\frac{1}{2}$) bound at a defect with nuclear spin $I=\frac{1}{2}$ of 100% natural abundance. It is obvious that P is the only realistic candidate which possesses these properties. The spin Hamiltonian for a localized paramagnetic defect is

$$H=\mu_B\mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}+\mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I}\,, \tag{2}$$

where the first term is the electronic Zeeman interaction and the second the hyperfine structure reflecting the interaction between the electronic and nuclear spins. Using Hamiltonian (2) we found $g=2.003$ and $A=981\times10^{-4}$ cm^{-1}. These spin Hamiltonian parameters are in excel-

lent agreement with those reported previously for P_{In} antisites at singly ionized charge state (P_{In}^{+}) by electron spin resonance, ODMR, and electron-nuclear double resonance studies in bulk LEC InP.[15–18]

It should be pointed out that this P_{In} antisite ODMR signal is only present in samples grown at temperatures lower than 350 °C. It becomes undetectable when the growth temperature is lower than 265 °C, due to very weak PL intensity in such samples. Such a decrease in PL intensity can be explained by the increasing nonradiative recombination in the presence of deep defects in high concentrations. This correlates very well with the trend of increasing electron concentration with decreasing growth temperature due to the introduction of deep defects, as was discussed above.

The P_{In} antisite ODMR spectrum shown in Fig. 3(a) corresponds to a 1–2 % decrease in the PL emission peaking at 0.8 eV as shown in Fig. 3(b). The presence of this 0.8-eV PL band is accompanied by the presence of shallow acceptors. It is believed to arise from a donor-acceptor pair (DAP) recombination[16] where the corresponding acceptor is related to Be; however, the donor is not the P_{In} antisite for the following reasons. First, there is no P_{In} antisite ODMR observed from sample 7 grown at 350 °C, though a similar 0.8-eV PL band is present in a similar strength as in samples 8, 9, and 10 grown at 300 °C–310 °C. The latter show a strong ODMR signal as presented in Fig. 3(a). Second, it is a negative ODMR signal, corresponding to a decrease in PL intensity, which in most cases indicates that an indirect process is involved. In fact, the DAP emission band directly related to the phosphorus antisite defect has been observed in bulk InP at much higher energies[18] (>0.9 eV) along with detection of the positive ODMR signal. In LT InP the presence of deep defects in high concentrations enhances nonradiative recombination and therefore decreases drastically the efficiency of the direct radiative DAP emission.

In the inset to Fig. 3(b) we illustrate how such an indirect carrier recombination process can affect the optical properties of the material. Since the defect which participates in the 0.8-eV radiative recombination process is not the P_{In} antisite, the nonradiative recombination process between the P_{In} antisite and the Be-related acceptor acts as a competing recombination channel for the photoexcited free carriers. A magnetic resonance transition between the magnetic sublevels of the P_{In}^{+} antisite enhances the process, thus resulting in a decrease of the 0.8-eV PL band. Our model clearly explains why the energy of 0.8 eV cannot be used to estimate the energy of the $P_{In}^{+/++}$ level position with respect to the valence band as proposed formerly.[15,16] In electron-irradiated InP two antisite defects have been identified.[18] It has been shown that the $P_{In}^{+/++}$ level of the isolated antisite is located in the upper half of the band gap at $E_V+(1.1\pm0.1)$ eV. Our determination of the energy position of the $P_{In}^{+/++}$ level at $E_\Gamma-0.22$ eV is in good agreement with the energy level $E_\Gamma-(0.3\pm0.1)$ eV, strongly indicating that the isolated antisites are dominant defects in LT InP.

In summary, by Hall and high-pressure far-infrared absorption measurements, we have shown that the electronic properties of the LT InP epilayers are determined by the presence of two dominant deep donor levels with energies at $E_\Gamma-0.22$ eV and $E_\Gamma+0.11$ eV. PL-ODMR experiments have shown the P_{In} antisite to be abundant in such LT epilayers. This defect is acting as an efficient nonradiative recombination center. Based on the correlation between the increase of the deep donor and therefore free carrier concentrations, and the appearance of the P_{In}^{+} ODMR signal, we conclude that these two donor levels arise from the phosphorus antisite double donor defect. To our knowledge, this is the first time the electronic structure of the P_{In} antisite defect has been positively identified.

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