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Optically detected magnetic-resonance study of Zn-doped InP: Nuclear-spin polarization at P_{In} antisites

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The antisite-acceptor recombination process in as-grown Zn-doped InP has been studied by optically detected magnetic resonance (ODMR) at 16.6 GHz. A model of dynamic polarization of P nuclei at the excited antisites ${P_{In}}^+$ by partially unthermalized antisite electron spins is proposed to explain the difference in the intensity of the two hyperfine lines of the antisite resonance. The trends of this difference with microwave and laser power are also studied. We suggest that nuclear spin polarization may be responsible for similar phenomena observed in a variety of ODMR spectra of antisite resonances.

INTRODUCTION

In the past decade, optically detected magnetic resonance (ODMR) experiments have identified antisite defects in a variety of III-V semiconductor alloys, such as InP, GaAs, and $Al_xGa_{1-x}As$.[1–4] The hyperfine multiplets in the ODMR spectra serve as a fingerprint of the antisite electron-spin resonance (ESR). In these works, an interesting phenomenon is observed but not understood in most cases:[3,4] the hyperfine multiplets are often not equal in their intensities with the higher-field components more intense than the lower-field components, a situation which is unusual compared with the ground-state ESR where the hyperfine lines have equal intensities.

In InP, the antisite P_{In} is a double donor. Under optical excitation, it is paramagnetic (${P_{In}}^+$) and observable by ODMR. Recently, Deiri *et al.*,[5] Robins, Taylor, and Ohlsen,[6] and Viohl, Taylor, and Kennedy[7] studied as-grown zinc-doped InP (InP:Zn) by ODMR and suggested a detailed rate equation model for the recombination processes upon magnetic resonance of the excited states in this material. In this model, the spin-thermalized shallow-donor electron and the spin-unthermalized phosphorus antisite electron compete to recombine with a spin-thermalized zinc acceptor hole. The recombination processes are radiative and yield photoluminesence (PL) at 1.37 eV for the shallow-donor-acceptor recombination and 0.87 eV for the antisite-acceptor recombination. The spin dependence of the recombination rates allows the detection of the magnetic resonances of the shallow-donor and antisite electrons by monitoring the intensity of either PL band.

This model explains correctly the sign of the ODMR signals (quenching or enhancing) and one modification[6] attributes the intensity inequality of the two hyperfine lines of the antisite resonance to the field dependence of the imbalance of the recombination rates of different spin states. However, we have found that the intensity ratio of the high-field component to the low-field component varies with the microwave power and laser excitation intensity and exceeds the limit that can be accounted for by the model of Robins, Taylor, and Kennedy.[6]

We suggest that there is an unrecognized common mechanism which plays a role in the inequality of the hyperfine lines in the ODMR spectra. The present work studies the P_{In} antisite resonance in as-grown InP:Zn under various experimental conditions and proposes a model of nuclear-spin polarization to explain the phenomenon mentioned above.

EXPERIMENTAL DETAILS

The sample used was a zinc-doped liquid-encapsulated-Czochralski-grown single crystal with a hole density of $\sim 10^{16}$ cm^{-3}. The experiments were performed on an ODMR spectrometer at 16.6 GHz. The microwave cavity and the sample were immersed in superfluid helium ($\sim$2 K). The microwaves were chopped by a *p-i-n* diode switch, typically at 300 Hz, to allow lock-in detection. The PL was excited perpendicular to the magnetic field by an Ar^+ laser operating at the 5145-Å line (2.4 eV), and the PL was collected perpendicular to the magnetic field (Voigt geometry). The strong shallow-donor-to-acceptor PL at 1.37 eV was collected by a cooled fast Ge detector (North Coast 817 P) through a 900-nm bandpass filter. The laser light was focused on a small area ($\sim$1 mm^2) of the sample where the microwave electric field is minimum to reduce the nonresonant microwave-induced background signal.[8,9] The laser intensity varied from 6 to 30 mW.

RESULTS AND DISCUSSION

The antisite resonances are observed as quenching signals on the 1.37-eV PL band. The relative change in the PL intensity upon resonance varies between 5×10^{-4} and 5×10^{-5} depending on the microwave power. The resonant fields for the antisite lines are measured to be 5350 and 6420 G at 16.6 GHz, which yield the spin-Hamiltonian parameters of $g\simeq2$ and $|A|\simeq0.1$ cm^{-1}. The hyperfine doublets have essentially the same linewidth, so the intensity ratio of the high-field line (I_h) to the low-field line (I_l) is simply the ratio of the peak amplitudes. This ratio is found to vary considerably with the applied microwave power. Figure 1 shows the ODMR spectra in two extreme cases where the mi-

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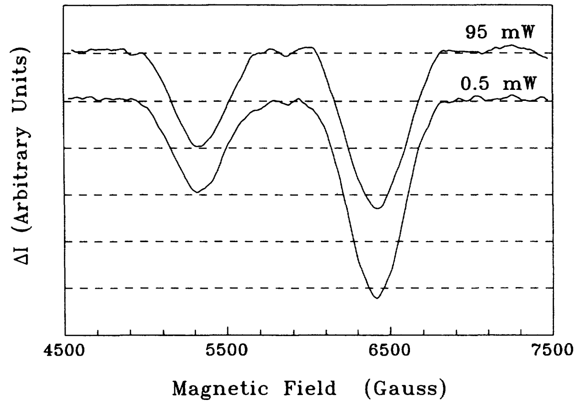

FIG. 1. ODMR spectra of P_{In} antisite on the 1.37-eV PL band at 16 GHz. The excitation intensity is 1 W/cm^2. The spectra were scaled so that the low field resonances have equal intensities. The traces are a result of the average of multiple scans.

crowave power is 95 and 0.5 mW, respectively. For the convenience of comparison, the spectra have been scaled so that the low-field lines have equal intensities. The ratio I_h/I_l as a function of the microwave power is displayed in Fig. 2, where one can see that the ratio I_h/I_l increases considerably from ~1.7 to ~2.2 as the microwave power is decreased from 100 to 0.5 mW. It is worth noting that the upper limit of the ratio I_h/I_l at 16 GHz suggested by Robins, Taylor, and Kennedy[6] is 1.47.

The possibility of a hidden resonance line overlapping the high-field component has to be examined here. Viohl, Taylor, and Ohlsen[7] observe at 3 GHz a resonance in InP:Zn with a g value of 1.85 and a linewidth of 600 G. At 16.6 GHz, this line would overlap the hyperfine line at 6420 G if the same resonance did exist in our sample. However, we exclude this possibility for two reasons. First, our careful study at 3 GHz under various experimental conditions shows no obvious signal at $g \simeq 1.85$ in the sample we have used. Second, the $g \simeq 1.85$ line found by Viohl and co-workers is more prominent under low excitation intensities[7] while the high-field line at 6420 G in our sample is more prominent under high excitation intensities (which we will discuss later).

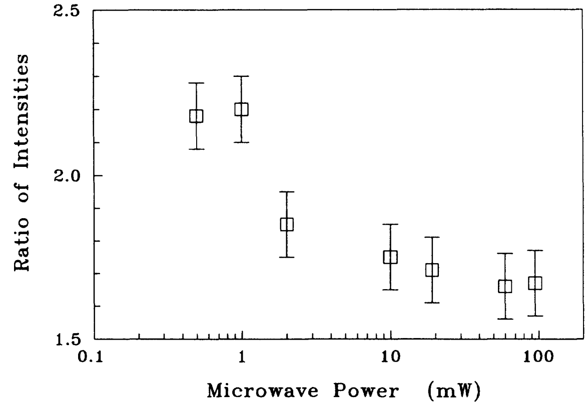

FIG. 2. The intensity ratio I_h/I_l of the high-field component to the low-field component as a function of applied microwave power. I_h/I_l increases from ~1.7 to ~2.2 as the microwave power is decreased from 100 to 0.5 mW. The laser intensity is kept constant at 1 W/cm^2.

The recombination model originally proposed by Deiri *et al.*[1] and later refined by Robins, Taylor, and Kennedy[6] and Viohl, Taylor, and Ohlsen[7] will be adopted in our discussion, and the nuclear-spin polarization effect will be incorporated to explain the difference in the magnitudes of the hyperfine lines.

In an external magnetic field $B = B_0\hat{z}$, the energy level of the antisite electron ($S=\frac{1}{2}$) is split into two sublevels and that of the acceptor hole ($J=\frac{3}{2}$) into four sublevels due to the Zeeman interaction. Neglecting the hyperfine interaction at this stage, the energy-level diagram is depicted in Fig. 3. The eigenstates are labeled by the z components of the angular momenta of the electron and hole $|m_e m_h\rangle$. The relative transition probabilities between each magnetic sublevel and the ground state ($J=0$, electrons and holes recombined) can be calculated in the electric dipole approximation and are shown in Fig. 3. The acceptor holes are assumed to be thermalized in this model, so the rates for the antisite-acceptor recombination (abbreviated by AN-AC hereafter) depend only on the spin state of the antisite electron. The AN-AC recombination rates for the spin-up (spin parallel to the B field) and spin-down electrons are given, respectively, by

$$V_{\uparrow} = \frac{1}{Z}(e^{-3x} + \tfrac{2}{3}e^{-x} + \tfrac{1}{3}e^{x})V , \tag{1}$$

$$V_{\downarrow} = \frac{1}{Z}(\tfrac{1}{3}e^{-x} + \tfrac{2}{3}e^{x} + e^{3x})V , \tag{2}$$

where $x = 0.5 g_h \mu_B B_0 / kT$, $Z = \sum_i e^{-E_i/kT}$, and V is the recombination rate in the absence of the magnetic field. By examination of Eqs. (1) and (2) it can be seen that spin-up electrons recombine more slowly (longer lifetime) than spin-down electrons. Because of the optical excitation geometry (Voigt geometry) the generation rates for

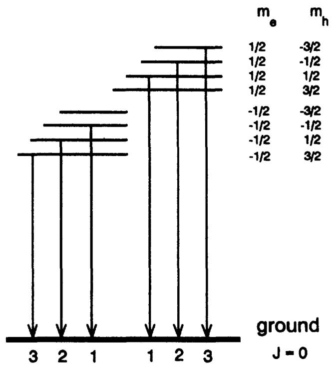

FIG. 3. The energy levels of the antisite-acceptor pair in a magnetic field B_0. The allowed electric dipole transitions and their relative probabilities are shown. The hole spins are assumed to be thermalized and the population of each sublevel is indicated by the length of the line representing that level.

spin-up and spin-down antisite electrons are likely to be the same. Let G be the generation rate for both states. The antisite electrons are assumed to be spin unthermalized,[7] i.e., the electron spin-lattice relaxation rate is negligible compared with the recombination rates, $V_\uparrow$ and $V_\downarrow$. The steady-state population would be $G/V_\uparrow$ and $G/V_\downarrow$ for spin-up and spin-down states, respectively. It is clear from this argument that the spin-up state, which is of higher energy, is more populated than the lower-lying spin-down state. Microwaves of the resonant frequency will stimulate microwave emission and depopulate the spin-up state.

When the hyperfine interaction between the phosphorus nucleus and the antisite electron is taken into account, the spin Hamiltonian is given by

$$\mathcal{H}=g_e\mu_B\mathbf{S}\cdot\mathbf{B}_0+A\mathbf{S}\cdot\mathbf{I}\ , \tag{3}$$

where S and I are the spins of the electrons and of the antisite P nucleus, respectively. For a phosphorus nucleus, $I=\frac{1}{2}$. There is an uncertainty of the sign of the hyperfine constant A. Recent measurements of the Overhauser shift of the conduction electron-spin resonance in InP yield the hyperfine interaction constants between the conduction electrons and the nuclei (In and P) on the regular lattice sites, and the relative sign of A with respect to g_e.[10,11] Unfortunately, the same sign cannot be assumed for the $\mathrm{P_{In}}^+$ antisites. Since the electronic wave functions are different in the two cases, the associated core polarization contributions will also be different. The core polarization contribution to the hyperfine interaction involves the differences of large terms of opposite sign for both the 1S and 2S shells of phosphorus. These near cancellations are so delicate that theoretical calculations for what is perhaps the simplest case, atomic phosphorus, have resulted in both positive and negative A values.[13–16] No calculation or experimental value is available for the sign of A for the $\mathrm{P_{In}}^+$ antisites in InP. For reasons explained later we assume that A is negative.

Figure 4(a) shows the hyperfine levels of the $\mathrm{P_{In}}$ antisite when the Zeeman interaction is much stronger than the hyperfine interaction and A is assumed to be negative. Let R_{ij} be the spin-lattice relaxation rate between levels $|i\rangle$ and $|j\rangle$. As discussed before, the electron spin-lattice relaxation rates R_{12} and R_{34} are assumed to be insignificant compared with the much faster recombination rate. The nuclear spin-lattice relaxation rates R_{13} and R_{24} are probably even weaker and are therefore negligible. The relaxation processes between $|1\rangle$ and $|4\rangle$ $[\Delta(M_S+m_I)=0]$ and between $|2\rangle$ and $|3\rangle$ $[\Delta(M_S+m_I)=2]$ involve flipping of both the electron spin and the nuclear spin simultaneously. It is these slow processes that can build up the nuclear-spin polarization.[12]

The observed differences in intensities between the two hyperfine lines as shown in Fig. 2 can be explained consistently by reasonably assuming that R_{14} is much stronger than R_{23}. In this case, one can neglect R_{23} and the relaxation process R_{14} will increase the population of $\mathrm{P_{In}}$ nuclei in the spin-up state ($n_\uparrow$) at the expense of that of the spin-down state ($n_\downarrow$). This process increases the nuclear-spin polarization until thermal equilibrium is established between $|1\rangle$ and $|4\rangle$. It should be noted that the net nuclear-spin polarization is not built up within one single lifetime of an AN-AC pair because R_{14} is probably much weaker than the recombination rates $V_\uparrow$ and $V_\downarrow$. Instead, the observed asymmetry in the hyperfine components is the accumulated result of the continuous polarization by antisite electrons over many excitation and recombination cycles of the AN-AC pair. A key factor in the polarization is that the $\mathrm{P_{In}}$ nucleus maintains its spin orientation after the AN-AC pair recombines due to the long nuclear spin-lattice relaxation time (T_1). In fact, T_1 is measured to be 310±15 s at 4.2 K for ^{31}P in InP.[10]

Nuclear-spin polarization is also suggested by the results of an optically detected electron-nuclear double resonance (ODENDOR) experiment on InP by Jeon *et al.*[17] These authors have observed a change of 30–45 % in the ODMR signal associated with the resonance of the neighboring P nuclei. For an unpolarized ensemble of nuclear spins, the effect would be much smaller.

With the model developed above, it can be understood that there are more spin-up antisite P nuclei than spin-down P nuclei. The low-field antisite resonance, which corresponds to the minority nuclear–spin-down state, therefore has less intensity than the high-field resonance, which is related to the majority nuclear–spin-up state [Fig. 4(b)]. The reader is reminded that the polarization

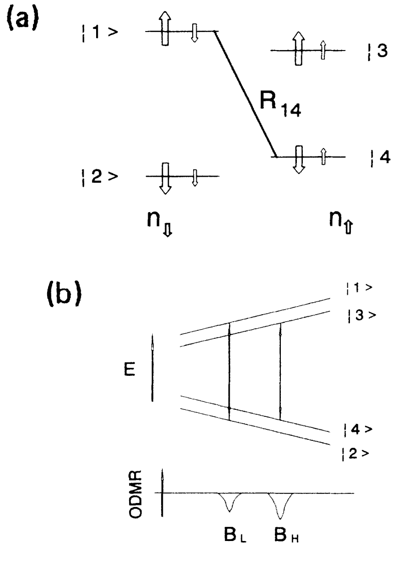

FIG. 4. (a) The hyperfine levels of the $\mathrm{P_{In}}$ antisite when the Zeeman interaction is much stronger than the hyperfine interaction. The spin states are indicated by a large arrow for the electron and a small arrow for the nucleus. $n_\uparrow$ and $n_\downarrow$ denote the fraction of $\mathrm{P_{In}}$ nuclei in spin-up and spin-down states, respectively. Spin-lattice relaxation between $|1\rangle$ and $|4\rangle$ is assumed to be the process that builds up the nuclear-spin polarization. (b) ODMR of the $\mathrm{P_{In}}$ antisite. The low-field resonance is between $|1\rangle$ and $|2\rangle$ and the high-field resonance between $|3\rangle$ and $|4\rangle$. Due to the field dependence of the recombination rates and the nuclear-spin polarization, the high-field line is stronger than the low-field line.

that favors the spin-up states is a direct result of our *ad hoc* assumption that the hyperfine coupling constant A is negative. If we had assumed a positive A value, it would require that the relaxation between levels $|2\rangle$ and $|3\rangle$ build up the nuclear-spin polarization. This situation appears to be less likely because $\Delta(M+m)=2$ in this case while $\Delta(M+m)=0$ for relaxation between levels $|1\rangle$ and $|4\rangle$. ODMR studies, where changes in the absorption are monitored for electronic $S>1/2$, indicate that "anomalous" situations can exist where the forbidden optical transitions appear to be more rapid than the allowed transitions. Such anomalous relaxation has been observed for Mn^{2+} in GaAs.[18] Because this situation is anomalous, we believe it is a less likely explanation of the ODMR data in InP.

We now estimate the intensity ratio I_h/I_l at low microwave power within the context of this model. At low microwave power, the steady-state population is assumed to be undisturbed by the microwaves. Let n_i $(i=1,\ldots,4)$ be the relative population in the level $|i\rangle$, G the generation rate, $V_\uparrow$ and $V_\downarrow$ the recombination rates for electron spin-up and spin-down AN-AC pairs, respectively, and $n_\uparrow$ and $n_\downarrow$ the fractions of $\mathrm{P_{In}}$ with the nuclear spins up and down, respectively $(n_\uparrow+n_\downarrow=1)$. Each fraction n_i is proportional to the product of G and either $n_\uparrow$ or $n_\downarrow$, and inversely proportional to either $V_\uparrow$ and $V_\downarrow$, as appropriate. If there is complete thermalization between states $|1\rangle$ and $|4\rangle$, then

$$\frac{N_1}{N_4}=e^{-(E_1-E_4/kT)}=\alpha \; . \tag{4}$$

In reality, Eq. (4) may only be approximately correct. With this assumption, the ratio I_h/I_l is found to be

$$\frac{I_h}{I_l}=\frac{\left[\dfrac{\mu^2}{1-\mu^2+(1-\mu)^2\alpha}\right]_h}{\left[\dfrac{\alpha\mu^2}{(1+\mu)^2+\alpha(1-\mu^2)}\right]_l} \; , \tag{5}$$

where $\mu=(V_\downarrow-V_\uparrow)/V$ and the subscripts h and l indicate the resonant field at which the expression is to be evaluated (high or low). Using the known antisite spin-Hamiltonian parameters and assuming a hole g_h value of 0.76,[19–21] one finds that $I_h/I_l\simeq 2.7$.

At high microwave power, the populations of the energy levels connected by the microwaves tend to be equalized upon resonance. The maximum I_h/I_l is calculated to be 2.4 in this power region. The smaller values of I_h/I_l can be qualitatively understood if one realizes that the microwaves depopulate level $|1\rangle$ (or level $|4\rangle$), thus reducing the degree of nuclear polarization.

The experimental value of I_h/I_l measured in the present study varies from 2.2 ± 0.1 at low microwave power to 1.5 ± 0.1 at high microwave power. The functional dependence of I_h/I_l on the microwave power is therefore consistent with the present model. It should be noted that 2.7 and 2.4 are the absolute upper limits for I_h/I_l in the two microwave power regions. In reality the measured I_h/I_l could be smaller because of at least two factors: (1) the full nuclear-spin polarization may not be achieved if the relation rate R_{23} is comparable to the rate R_{14}; (2) the antisite electron is only partially thermalized as has been suggested by previous ODMR experiments.[6]

We found that the ratio I_h/I_l also depends on the excitation intensity, and higher excitation intensity results in a larger value of I_h/I_l for constant microwave power. For example, the ratio I_h/I_l increases from ~ 1.8 to ~ 2.1 as the laser intensity is increased from 10 to 30 mW for a microwave power of 4.5 mW. This trend can be understood within the context of the present model as an increase in the degree of nuclear polarization since within a given period of time there are more AN-AC pair excitation and recombination cycles at higher excitation laser intensity and the possibility of polarizing P antisite nuclei is increased.

CONCLUSION

The antisite-acceptor recombination process in as-grown Zn-doped InP has been studied by optically detected magnetic resonance (ODMR) at 16.6 GHz. A model of dynamic polarization of P nuclei at the excited antisites ${\mathrm{P_{In}}}^{+}$ by partially unthermalized antisite electron spins is proposed to explain the difference in the intensity of the two hyperfine antisite resonance lines. The experimental results agree well with the calculated ratios of intensities. This proposed explanation depends on two assumptions, the assumption that the Zn acceptors are thermalized while the $\mathrm{P_{In}}$ antisites are unthermalized, and the assumption that the hyperfine coupling constant A is negative for the $\mathrm{P_{In}}$ antisite. Both assumptions require further justification.

It is possible that the nuclear-spin polarization may also be responsible for similar phenomena observed in other ODMR experiments of antisite resonances in GaAs, $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$, and other III-V semiconductors.[3,4] Experimental evidence for this generalization is an ODENDOR study of the $\mathrm{As_{Ga}}$ antisite in GaAs,[22] where the ODENDOR effect is of the same order of magnitude as the ODMR effect.

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