Brief Reports

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Time-sequenced optical nuclear magnetic resonance of gallium arsenide

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A method of optical detection of nuclear magnetic resonance is demonstrated in which optical nuclear polarization, spin resonance, and optical detection are separated into distinct sequential periods and separately optimized by varying the optical, rf, and static fields. Experiments on the bulk ^{69}Ga resonance of GaAs show that sites imperceptibly perturbed by the optically relevant defect are optically observable with the rf applied in the dark. A signal-to-noise analysis is given that relates the sensitivity to readily measured material properties and indicates applicability to dilute defects.

Solid-state nuclear magnetic resonance (NMR) spectroscopy has been a premier tool for the determination of structure. For solids the usual method, Larmor frequency detection of equilibrium spin magnetization, typically requires samples of $\cong 1$ cm^3. Even then, NMR is too insensitive to use for defect identification in III-V semiconductors with defect concentrations below 10^{18}/cm^3.[1] An effective mechanism for coupling nuclear magnetization to the optical spectroscopy of these materials has been extensively studied[2–18] and used to obtain (quasi-) steady-state NMR spectra in $Ga_{1-x}Al_xAs$,[10–12] GaAs,[12–16] and, recently, in quantum wells formed from these materials.[17,18] Here we demonstrate in p-type GaAs an alternative method, time-sequenced optical NMR, that dramatically improves both sensitivity and resolution.

Several distinct spectroscopic processes are involved in the optical NMR of GaAs. In the present method they occur in three distinct intervals. In the first step optical nuclear polarization is induced by irradiation with circularly polarized light near the band gap in an external magnetic field $\mathbf{B}_0^p$ parallel to the direction of light propagation. The optical selection rules create an electron spin polarization $\mathbf{P}_e = 2\langle \mathbf{S} \rangle$, which is ≤ 0.5 in bulk GaAs (Refs. 2 and 3) and can approach unity in quantum wells.[17,18] This leads to a large steady-state nonequilibrium nuclear polarization which is approached with time constant T_{1on} (seconds to minutes). The subscript denotes spin-lattice relaxation with the band-gap light on. This process only requires B_0^p to be greater than the internuclear dipolar couplings, but will typically be optimum in high field,[4,11,12] where the electron spin-lattice relaxation rate $1/\tau_s$ falls well below the decay rate $1/\tau$ of the optically excited states.

In the second step the light is turned off and the nuclei are irradiated as in any NMR or nuclear quadrupole resonance experiment. For the purposes of discussing the present experiments, a single rf frequency variable ω will distinguish successive repetitions of the sequence, but multiple resonance and time-domain experiments could be treated identically. Since T_{1off} is at least as long as T_{1on} and can be many minutes,[11,14] it is practical to cycle adiabatically to any field $\mathbf{B}_0^n$, possibly different from $\mathbf{B}_0^p$, appropriate for the nuclear resonance. The absence of the light during the rf irradiation step will be shown to be crucial to spectral resolution and interpretation.

The third step is optical detection of the remaining nuclear polarization (ODNMR). Depending on the material's selection rules, similar to those that lead to the optical pumping, the electron spin polarization along the direction of light propagation is either equal to[2,3] or is twice[17,18] the experimentally observed circular polarization of luminescence, $\rho = (N_+ - N_-)/(N_+ + N_-)$, detected along this axis. Here $N_\pm$ is the number of right-hand and left-hand photons counted, respectively.

The observable ρ can report on the nuclear polarization by two distinct mechanisms, both of which are conveniently discussed in terms of the nuclear field B_n,[4,10–13] the average hyperfine interaction of the emitting states. The first mechanism is the dependence of τ_s on the total field $\mathbf{B}_T = \mathbf{B}_0 + \mathbf{B}_N$.[4,10,11] The more effective mechanism used here is a type of Hanle effect,[5,11,12] the depolarization of the optically pumped electron spins by precession about $\mathbf{B}_T$. Because the optical lifetime τ ($\cong 10^{-10}$–10^{-9} s) is much shorter than both the measurement period for ρ and the time for nuclear reorientation, the relevant electron spin polarization is given by the steady-state solution of the Bloch equation for a given $\mathbf{B}_T$. The role

of this Hanle effect in (quasi-) steady-state ODNMR, where $\mathbf{B}_0$ remains along the z axis and $\mathbf{B}_N$ is tilted by resonant irradiation, has been discussed in detail.[11,13,17] The NMR line shapes observed in this way are at least 1 mT in width, due to the broadening by the electron hyperfine field of the photocarriers,[5,13] and are also power broadened and distorted under conditions that optimize sensitivity.

For the time-sequenced experiment this incompatibility between sensitivity and resolution is reconciled. We need only consider the case where $\mathbf{B}_0$ and $\mathbf{B}_N$ are collinear (parallel or antiparallel) and perpendicular to the direction of light propagation z. This is achieved by rotation of $\mathbf{B}_0$ into the x direction with $\mathbf{B}_N$ following adiabatically. The observed transient determined by the quasi-steady-state Hanle effect subsequent to restoring the light at $t_d=0$ is given by

$$\rho(\omega,t_d)=\frac{C^2\tau_s\Delta B^2}{(\tau+\tau_s)[\Delta B^2+B_T^2(\omega,t_d)]}\ , \tag{1}$$

where $\Delta B=h(\tau+\tau_s)(\tau\tau_s|g^*|\mu_B)^{-1}$ is the Hanle width and $C^2=0.25$ for the bulk selection rules or $C^2=1$ for quantum wells. The time dependence[9] is due to the approach to a steady-state nuclear field B_N^d under the influence of the detection period applied field $\mathbf{B}_0^d=B_0^d\mathbf{x}$, the optical irradiation and other spin-lattice mechanisms.[5,19] The nuclear field is approached exponentially starting from the value $B_N(\omega)$, which survives the NMR irradiation at frequency ω in the dark. Thus insertion of $B_T(\omega,t_d)=B_0^d+B_N^d+[B_N(\omega)-B_N^d]\exp(-t_d/T_{1on})$ into Eq. (1) specifies the transient.

The sample is p-type GaAs with $4\times10^{17}/\text{cm}^3$ Zn, grown by molecular-beam epitaxy. The timing and fields are sketched in Fig. 1(a). The sample is irradiated at 790 nm with $\cong$20 W/cm^2 from a diode laser (Spindler and Hoyer model DC25C) for 30 s in a z-axis field $B_0^p=15$ mT. The light is shuttered and after rf irradiation for 100 ms the external applied field is adiabatically cycled to an x-axis field $B_0^d=3$ mT in about 1 s by simultaneously turning one electromagnet off and an orthogonal one on. The irradiation is restored and the circular polarization of the undispersed luminescence is measured for several seconds by two-channel gated single-photon counting[20,21] (Stanford Research Systems SR400) of the output of a 50-kHz photoelastic modulator (HINDS Intl. model PEM-80) and linear polarizer with an avalanche photodiode (RCA C30902S, used in Geiger mode with a detected quantum efficiency equal to 7.7%). The sample is held at 77 K in liquid N_2.

Figure 1(b) is an experimental example of this procedure omitting the rf irradiation and serves as a null for the NMR experiment. The fit according to Eq. (1) provides the parameters $\Delta B=7.5$ mT, $B_N^{\text{null}}=4.0$ mT, $B_N^d=0.0$, and $T_{1on}=2.0$ s.

The time-sequenced NMR signal $S(\omega)$ is the frequency-dependent modulation in the area of the transient $\rho(t_d)$. Figure 2(a) is a demonstration of time-sequenced optical NMR on the ^{69}Ga resonance. The rf field strength was $\cong1$ μT and lower values gave the same linewidth of 2 ± 0.5 kHz. This is a factor of $\cong$20 narrower than the highest resolution spectrum of this resonance previously obtained with optical methods.[10,11] It is identical to the conventional NMR linewidth and is explicable as due to nuclear spin-spin coupling.[22,23]

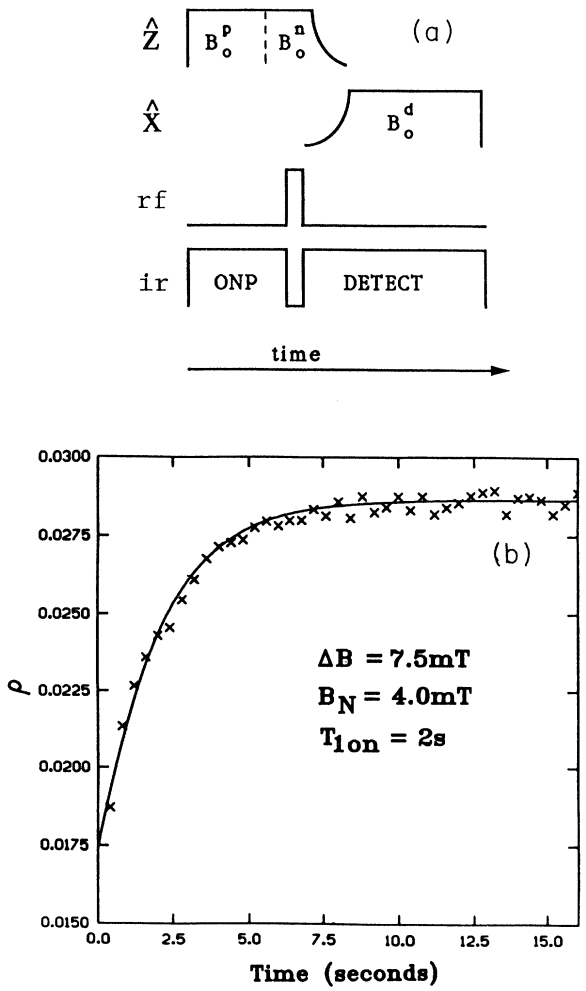

FIG. 1. The general timing diagram for (a) time-sequenced optical NMR and (b) the detected transient $\rho^{\text{null}}(t_d)$. The $\times$'s represent the data obtained from the experiment described in (a) omitting the rf irradiation. The solid line represents a theoretical fit, and the resulting parameters are given in the inset of (b).

Figure 2(b) is obtained identically, except that the light was not shuttered off during the NMR period. The resonance shifts 6 ± 1 kHz downfield and the linewidth increases to 6 kHz. This is readily understood as a Knight shift of 0.6 mT due to the polarized photocarriers. This interpretation is strengthened by noting that this same value is obtained by multiplying the experimentally observed value of $\rho=\langle S_z\rangle=0.033$ by a theoretical estimate of the electron hyperfine interactions of 17 mT.[5] The broadening of the "light-on" resonance is presumably due to inhomogeneities in the electron field.

The hyperfine coupling responsible for the effectiveness of both the optical nuclear polarization and the Hanle-

effect detection is understood both from theoretical estimates[5] and from experimental observations of the polarization dynamics[13] to be due to localization of the photocarriers into defect states of unknown chemical identity having a Bohr radius of $\cong 10$ nm. The present results are consistent with this interpretation, but sharpen it in a way that is encouraging for analytical uses of the method. While the "light-on" spectrum of Fig. 2(b) shows that the signal is dominated by nuclear spins that experience the optical Knight shift, the "light-off" resonance shows that these spins have a spectrum that in the absence of photocarriers is not measurably perturbed by the optically relevant defect. Thus it is anticipated that the method will be applicable to randomly distributed defects and that the necessary proximity to a localization site will not unduly degrade the resolution. A similar situation might be expected to hold in quantum wells,[17,18] where the interfacial barrier provides the necessary electron localization and point defects are presumably unnecessary.

The signal-to-noise ratio in Fig. 2 is consistent with quantum-limited detection and a change in the nuclear field $\delta B_N(\omega)=[B_N(\omega)-B_n^{\text{null}}]\cong 0.02B_N$ by the NMR irradiation at resonance. It corresponds to a volume of $\cong 10^{-7}$ cm^3 implying sensitivity about five orders of magnitude better than conventional NMR. This estimate is self-consistent in that it represents a destruction of $\cong 8\%$ of the ^{69}Ga polarization (which represents 26% of the total nuclear field[5]) and a significantly higher percent destruction would be expected to be associated with power broadening and overtone transitions,[15] which were indeed seen at higher rf field strength. Also, in separate measurements in which the rf frequency was not incremented, the variance in the observed signal was that expected from the photon statistics and this value is indicated by the error bar in Fig. 2(a).

For defect studies it is evident that much better sensitivity is desirable. This will be possible with improvements in the apparatus, the method, and the samples. In order to quantify these factors a sensitivity analysis and optimization is needed for the marginal case of small changes $\delta B_N(\omega) \ll \Delta B$. Letting $\mathcal{N}$ be the photon counting rate and including a weighting function $W(t_d)=\exp(-t_d/T_{1\text{on}})$ to minimize noise, the signal may be defined as

$$S(\omega)=\mathcal{N}\int_0^\infty [\rho(\omega,t_d)-\rho_{\text{null}}(t_d)]W(t_d)dt_d \ . \tag{2}$$

The difference in the integrand will be optimized when the magnitude of B_0^d and the relative sign of $B_N(\omega)$ have been chosen to satisfy $B_T\cong\Delta B/\sqrt{3}$, which maximizes the slope $d\rho/dB_T$. For $B_N \gg \Delta B$, maintaining this condition will require that the detection field follow the decay of the nuclear field, i.e., $B_0^d=B_0^d(t_d=0)\exp(-t_d/T_{1\text{on}})$. With this substitution and the definition $d(\omega)\equiv\delta B_N(\omega)/B_N$ as the fractional destruction of the nuclear hyperfine field by the resonant irradiation, Eqs. (1) and (2) lead to

$$S_{\max}(\omega)=-\left[\frac{3\sqrt{3}}{8}\right]\mathcal{N}C^2\tau_s\left[\frac{1}{\tau+\tau_s}\right]\left[\frac{d(\omega)B_N}{\Delta B}\right]T_{1\text{on}} \ . \tag{3}$$

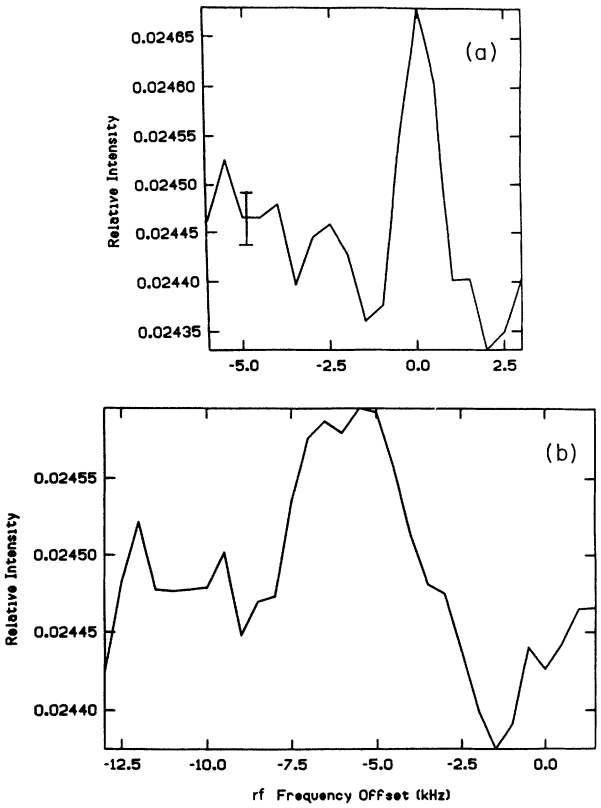

FIG. 2. Time-sequenced optical NMR of ^{69}Ga in GaAs. The spectra in (a) and (b) were obtained with the light off and the light on during NMR, respectively. The x axis in (a) is identical to and aligned with the x axis in (b). The difference in the resonance frequency for the two spectra is due to the optical Knight shift of $\simeq 6$ kHz. The broadening of the resonance in (b) is due to inhomogeneities of the electron field B_e.

Under conditions of quantum-limited noise due to photon statistics, the uncertainty in this value (per root repetition) is equal to the square root of the effective number of photons, $N_{\text{eff}}\equiv\mathcal{N}\int_0^\infty W(t_d)dt_d\cong\mathcal{N}T_{1\text{on}}$.

The material parameters appearing in our sensitivity analysis for the time-sequenced experiment have been measured in steady-state experiments,[5,11,17] allowing the potential signal-to-noise ratio for other systems to be estimated. The most striking observation in this regard is that in samples for which the less sensitive steady-state optical NMR experiments have been demonstrated[5,11–13] nuclear fields up to several tesla have been cited. Thus the present time-sequenced experiments succeeded with three orders of magnitude smaller nuclear field. This small value is not unexpected, as a decrease in nuclear field with donor concentration in p-type GaAs is well known.[5,12,24] In addition, luminescence count rates substantially higher than the present $\cong 5\times 10^5$ counts/s will be possible with other detectors and sources.

In addition to increasing B_N and measuring it more accurately, there is also room for sensitivity improvement by amplifying the fractional change $d(\omega)$ produced by a given resonance. A variety of such methods are

known,[25–28] which have in common that the depolarization of many abundant spins is arranged to occur when resonance is achieved with a dilute target spin. Time-sequenced optical NMR is uniquely suitable for combination with such methods, since rapid optical nuclear polarization can be combined with long spin-lattice relaxation times in the dark. Thus several additional orders of magnitude of enhancement are anticipated, making possible the spatially resolved study of surface or interfacial sites and of bulk defects at below ppm levels.

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