Surface-sensitive NMR in optically pumped semiconductors

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Abstract We present a scheme of surface-sensitive nuclear magnetic resonance in optically pumped semiconductors, where an NMR signal from a part of the surface of a bulk compound semiconductor is detected apart from the bulk signal. It utilizes optically oriented nuclei with a long spin-lattice relaxation time as a polarization reservoir for the second (target) nuclei to be detected. It provides a basis for the nuclear spin polarizer [IEEE Trans. Appl. Supercond. 14, 1635 (2004)], which is a polarization reservoir at a surface of the optically pumped semiconductor that polarizes nuclear spins in a target material in contact through the nanostructured interfaces.

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1 Introduction

Spatial resolution is one of the key ingredients in nanoscale characterizations. Nuclear magnetic resonance (NMR), which is a powerful analytical tool to investigate structural and dynamical properties of materials, is less advantageous in this respect. To gain high spatial resolution in NMR, one needs to invoke some characteristic systems that are specially designed for this purpose. Examples include magnetic resonance imaging microscopy\textsuperscript{1} and magnetic resonance force microscopy,\textsuperscript{2} where high spatial resolution is achieved by a strong magnetic field gradient that surpasses NMR line widths. This requirement, as well as that for high sensitivity to detect small number of nuclei in a small region, has posed serious challenges to these techniques.

In some cases, it is possible to identify signals from a part of a bulk material even in the absence of field gradients, by making use of the structural features. For example, at interfaces in composite materials, nuclear polarization can be transferred from one material to another. In this case, the transferred nuclear polarization is localized in proximity to the interfaces within the nuclear spin diffusion length, so that one can selectively detect NMR signals from that area. This can be referred to as interface-sensitive NMR. The method is often combined with dynamic nuclear polarization or optical pumping. Examples include solid surfaces adsorbed by hyperpolarized $^{129}$Xe gas\textsuperscript{3,4,5}, solvents in dynamically polarized solutions\textsuperscript{6} and interfaces between solid materials and semiconductors.\textsuperscript{7,8}

Our current interest resides in the last case, especially that combined with the optical pumping.\textsuperscript{9} We proposed a nuclear spin polarizer (NSP) as a possible configuration of this kind,\textsuperscript{10,11} which utilize the successive polarization transfer scheme shown in Fig. 1. It is intended to enhance signals from a surface of a (tar-

![Fig. 1 Successive polarization transfer process in a compound semiconductor (with I and S nuclei) and a ‘target’ material (with $S_t$). Initial polarization is provided by circularly polarized photons, which excite polarized electrons at a surface of the semiconductor. The electrons polarize I nuclei nearby via hyperfine couplings, and the I nuclei polarize S via heteronuclear couplings. As a result, enhanced $S_t$ signals from the illuminated area are detected (surface-sensitive NMR). The polarization is further transferred to $S_t$ across the interfaces, and enhanced $S_t$ signals in the target material are detected (nuclear spin polarizer). In these processes, signals from the nuclei located deep in the bulk (gray spheres) are cancelled out and do not contribute to the signal detected.](image-url)
target) material to which conventional dynamic nuclear polarization techniques are inapplicable. With the aid of an optically oriented semiconductor, nuclei in the target material are indirectly polarized. Examples of the target include nano-structures built on semiconducting bulk materials, such as quantum dots on substrates. A typical configuration of the scheme is depicted in Fig. 2.

2 Surface-sensitive NMR

Here, we introduce a possible variation of the nuclear spin polarizer, i.e., surface-sensitive NMR in optically pumped semiconductors. Target nuclei (S) are located at a surface of a bulk compound semiconductor, whose signals are detected apart from those in the rest of the material. A key feature of the scheme is that it utilizes the primary nuclei (I) with a long spin-lattice relaxation time $T_1^I$ (as is often the case in semiconductors) as a polarization reservoir for the secondary (target) nuclei (S) to be detected, which enables us to detect S signals from the illuminated area selectively, as illustrated in Fig. 3. This is in contrast to the conventional (bulk) NMR in a uniform magnetic field, where nuclei in the whole sample are excited and detected.

The pulse sequence of the scheme is shown in Fig. 4 together with the time dependence of the I and S polarizations in both the illuminated area and the rest of the sample (bulk). The sequence consists of the four processes. (1) Saturation (SAT): comb pulses made of trains of 90°-pulses are applied to both the nuclei to extinguish the initial polarizations in thermal equilibrium. (2) Optical pumping (OP): the infrared light is irradiated for the effective duration time of $\tau_L$ to create polarizations in the illuminated area. In this period, the S polarization in the bulk may recover toward its thermal equilibrium value with the time scale of $T_1^S$, while that of I does not because $T_1^I$ is much longer than $\tau_L$. (3) Cross polarization (CP): the second SAT pulse is applied for S, which is followed by a cross polarization between I and S. The CP promotes polarization transfers in the illuminated area, but not in the bulk because the I polarization is absent there. (4) Signal acquisition (ACQ): only the S signal in the illuminated area is detected in the final signal acquisition process.
3 Surface-sensitive NMR in InP

We have previously reported successive polarization transfer experiments in indium phosphide. Here, we discuss the results in the context of the surface-sensitive NMR. The sample used was a 350 \( \mu \)m-thick wafer of the semi-insulating iron-doped InP with the crystal orientation of (100) and the carrier density at room temperature \( n = 7 \times 10^{17} \) cm\(^{-3}\). It was set with the surface normal to the magnetic field and a light beam.

Figure 5 shows three Fourier-Transform spectra of \(^{115}\)In at 6.346 T and 10 K. The spectrum (a) was obtained with the sequence SAT\( - \tau_L - (90^\circ)_x - \)FID without IR irradiation, which represents a bulk \(^{115}\)In signal in thermal equilibrium. The spectrum (b), on the other hand, was obtained with the sequence shown in Fig. 3 with \( I = ^{31}\)P, \( S = ^{115}\)In and \( \tau_L = 120 \) s. The wavelength \( (\lambda) \) and helicity \( (\sigma^\pm) \) were set at 890 nm and \( \sigma^+ \), respectively, where the largest optical orientation effects were observed in both \(^{31}\)P and \(^{115}\)In. Since the photon energy is below the band gap, the penetration depth of the light may be as thick as a few tens of \( \mu \)m. 

The relaxation time (\( T_1 \)) and the buildup time (\( T_b \)) times were reported to be \( T_1^S \approx 0.1 \) s, \( T_1^I \approx 10^3 \) s and \( T_b^S \approx T_b^I \approx 10^3 \) s, hence the condition \( T_1^I \gg T_b^I \) is satisfied. As a result, transfer from the bulk \( I \) spins is absent and the spectrum (b) represents only the signal from the illuminated area, as explained in Fig. 4(b).

The spectrum (c) was obtained with the same sequence as (b) but without light irradiation. Since no polarization grows during \( \tau_L \), no signal intensity is observed in (c).

The total efficiency of the scheme, which is evaluated by the polarization of the target nuclei, is maximized by optimizing each of the polarization transfer processes. In the cross polarization process, the transferred polarization is generally expressed as,

\[
M_S(\tau_{cp}) \propto \left[ 1 - \exp\left( -1 - \frac{T_{IS}}{T_{1_P}}\frac{\tau_{cp}}{T_{IS}} \right) \right] \exp\left( -\frac{\tau_{cp}}{T_{1_P}} \right),
\]

where \( T_{IS} \) and \( T_{1_P} \) are the cross-relaxation time between \( I \) and \( S \) and the relaxation time of \( I \) in the rotating flame, respectively. As is evident from (1), the cross-relaxation time \( (T_{IS}) \) should be faster than the relaxation time \( (T_{1_P}) \) to minimize transfer loss during the cross polarization process.

The present material (iron-doped InP) is fortunate in this respect. First, the relaxation in the rotation flame is negligible \( (T_{1_I} \rightarrow \infty) \) due mainly to the high crystal symmetry. Secondly, the cross relaxation time is rather fast under the optical pumping condition. It was reported to be \( T_{IS} = (1.1 \pm 0.1) \times 10^{-4} \) s, which is by an order of magnitude faster than that estimated for the nuclear dipolar couplings, because of the indirect \( J \)-couplings of the order of kHz. These result indicates that semi-insulating iron-doped InP is a good candidate for the nuclear spin polarizer.

4 Conclusion

In this article, we have described the scheme of the surface-sensitive NMR in optically pumped semiconductors and shown its feasibility with the example of InP wafers. 

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