Optically enhanced NMR of plastically deformed GaAs

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^{69}Ga and ^{75}As NMR of plastically deformed GaAs under optical pumping conditions at low temperatures is shown to exhibit substantial differences compared to results obtained from as-grown material. NMR signal enhancement has been observed in a wide energy range of the irradiation light above and below the band gap. The phase of the NMR signals is independent of the helicity of the pumping light. A continuum of intragap states introduced in the GaAs upon plastic deformation is involved in the polarization of the nuclei. [S0163-1829(97)12407-9]

Optically enhanced NMR in high magnetic field[1–3] and real-time optical detection in low magnetic field[4] are attracting increasing interest for the study of mesoscopic semiconductor materials, e.g., as a probe of the two-dimensional (2D) electronic structure in quantum wells. Substantial differences in the basic processes responsible for the signal enhancement in bulk GaAs and layered GaAs heterostructures have been pointed out recently.[5] In quantum wells, the signal enhancement was attributed to optical pumping of the Landau levels. In bulk GaAs, the direct population of shallow intragap localized states is dominant and the enhancement is effective only in a narrow frequency range just below the gap. The nuclear polarization produced in the vicinity of these shallow traps diffuses successively into the bulk. Spin diffusion is also observed in heterostructures, giving rise to distinguishable NMR signals of the wells and the barriers.[2,3]

In this contribution, we report an optically enhanced NMR study of plastically deformed GaAs. In this material, the enhancement occurs upon irradiation of a continuum of intragap states. This supports previous experimental evidence[5] that in 3D materials the enhanced nuclear polarization arises mainly from interaction with localized electronic states.

The GaAs crystal was uniaxially deformed at 400 °C along the [011] axis with a deformation load of 21.6 MPa, resulting in a deformation grade of $e=\Delta l/l=5.3\%$. During the cooling process, the deformation load was kept on the sample to prevent the crystal from stress relaxation through dislocation movement. The crystal was then characterized by optical absorption and electron paramagnetic resonance spectroscopy. The optical absorption experiments were carried out at 3 K. Experimental details are described elsewhere.[6]

Plastic deformation of GaAs introduces two classes of defects: extended structural defects, such as dislocations, and well-defined point defects. The dislocation density of plastically deformed crystals is typically in the range of 10^9 cm^{-2}, as compared to 10^4 cm^{-2} in as-grown materials.[7] Unambiguously identified point defects induced by plastic deformation are antisite defects that are paramagnetic in their singly ionized charge state. The densities of the arsenic antisite defect $As_{Ga}{}^{+}$ and the gallium antisite defect $Ga_{As}{}^{-}$ have been determined by EPR to be $[As_{Ga}{}^{+}]=4\times10^{16}$ cm^{-3} and $[Ga_{As}{}^{-}]=2.5\times10^{16}$ cm^{-3}, respectively.[8] For as-grown material we found $[As_{Ga}{}^{+}]=1.3\times10^{16}$ cm^{-3}, whereas the density of the gallium antisite is below the detection limit.

Figure 1 shows that the optical absorption spectrum of the deformed sample can be divided into two parts. One part is persistently photoquenchable at temperatures below 130 K and has been identified with the intracenter transition of the neutral charge state of the arsenic antisite defect As_{Ga}. Its concentration ($[As_{Ga}]=2\times10^{16}$ cm^{-3}) remains unaffected by deformation. The unquenchable background signal, however, increases with the deformation grade, as it has also been observed by Omling, Weber, and Samuelson.[9] The microscopic origin of this absorption has not been determined yet, but should be most likely attributed to either yet unidentified point defects or defect states associated with dislocation segments. With respect to NMR, the paramagnetic defects affect mainly the nuclear spin-lattice relaxation time, whereas dislocations introduce a large number of intragap states and may thus affect the optical transitions which are exploited in this work for the enhancement of the NMR signal.

The experimental setup for optically enhanced NMR has been described in detail in Ref. 5. For the detection of the NMR signals, a transmission line probe was tuned to the Larmor frequencies of ^{69}Ga and ^{75}As, 42.9 and 30.6 MHz, respectively. The Boltzmann equilibrium polarization was presaturated with a train of $\pi/2$ pulses. Then, the sample was irradiated with circularly polarized laser light for a period τ_L. Sample irradiation was timed with a shutter controlled by the pulse program of the NMR spectrometer. After a delay of 500 ms, a detection pulse was applied for data acquisition. For comparison, NMR signals without laser irradiation but otherwise same conditions were obtained and are referred to as ''dark'' signals. All experiments were performed in a cryostat at temperatures in the range $2\leqslant T\leqslant6$ K.

In Fig. 2, the optically enhanced NMR spectrum is shown together with the dark signal for ^{75}As and ^{69}Ga, respectively. Under the experimental conditions ($T=6$ K, 120 s equilibration time, and $T=2$ K, 60 s equilibration time, respectively), the spin-lattice relaxation time of ^{75}As and ^{69}Ga is so long (on the order of 10^3 s), that only a weak signal is observable without irradiation.

Figure 3 displays the dependence of the ^{69}Ga NMR signal intensity of the plastically deformed GaAs crystal on the energy of the incident light. For comparison, we also show the

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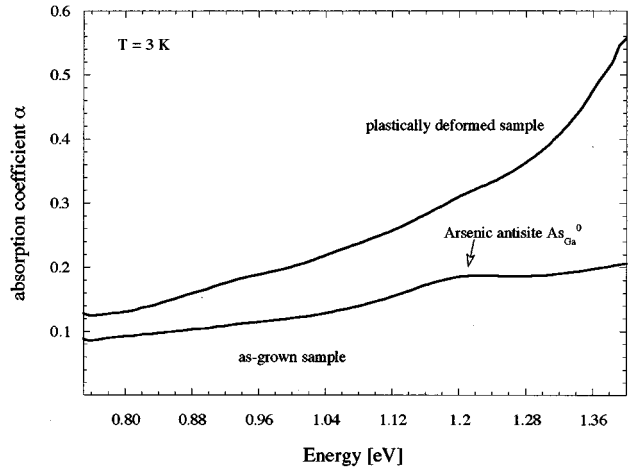

FIG. 1. Photoabsorption spectrum recorded at 3 K; comparison between plastically deformed and as-grown GaAs. (The spectrum is cut off at higher energies because the absolute absorption is below the detection limit of the Ge detector.) The distinct absorption band at 1.2 eV is caused by the intracenter transition of the neutral charge state of the EL2 defect.

same dependence for an as-grown GaAs crystal.[5] Peak positions and linewidths are the same for both the plastically deformed and the as-grown material. Whereas for the as-grown sample signal enhancement can only be observed in a narrow energy range just below the band gap,[5] for the plastically deformed crystal an enhanced NMR signal is observed in the whole range of investigation.

This difference can be correlated with the intragap states induced in the strained crystal by the plastic deformation. In as-grown GaAs, the nuclear-spin polarization enhancement upon optical excitation has been attributed to spin diffusion from localized shallow states.[5] This is consistent with the strongest signal enhancement just below the band gap caused by the presence of shallow traps and impurities, which may be favored due to the increased penetration depth of the laser light in this energy range. The large number of defects introduced into the band gap upon plastic deformation is most likely responsible for the broad energy range in which optical signal enhancement was observed. With increasing energy of irradiation light, a decrease in signal intensity was observed. This decrease is much less pronounced below the band gap than above the band gap. The transition, however, between the two regimes seems to occur at 1.50 eV, an energy slightly below the band gap at this temperature.[10] Above the band gap, the penetration depth of the irradiation light is limited to about 1 μm, whereas below the gap, the penetration depth grows with decreasing light energy. Thus, the decrease in signal intensity may be related to the smaller sample volume irradiated.

Uniaxial strain causes a splitting and a doublet shifting of the upper valence band Γ_8. Excitation of electrons from either of these subbands to the conduction band Γ_6 thus changes the maximum degree of spin orientation that can be achieved. The degree of orientation of the photoelectrons depends on the angle between the axis and the direction of the propagation vector of the light.[11] In our case, the light propagation was perpendicular to the deformation axis and transitions from this subband result in a spin orientation of

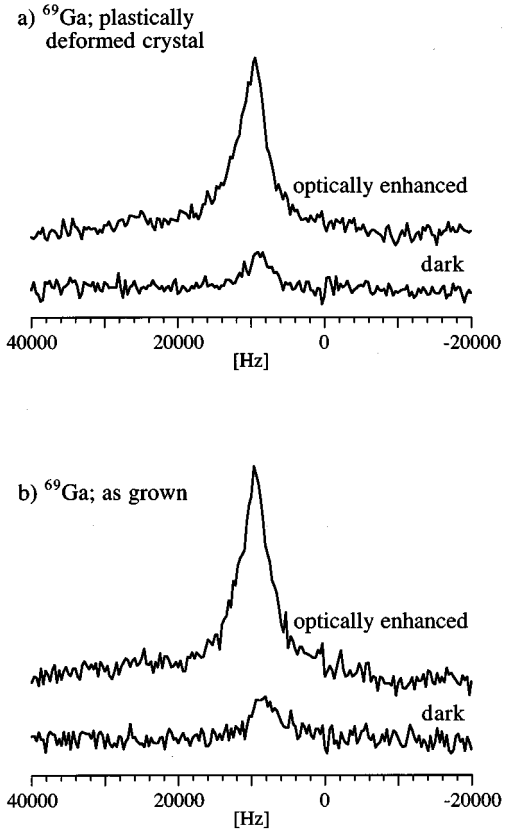

FIG. 2. (a) ^{69}Ga optically enhanced NMR spectrum of plastically deformed GaAs at 2 K and 1.49 eV light energy. Single pulse excitation (pulse width 11 μs). Irradiation time τ_L=120 s, laser power 900 mW. (b) ^{69}Ga optically enhanced NMR spectrum of as-grown GaAs at 2 K and 1.49 eV light energy. Single pulse excitation (pulse width 9 μs). Irradiation time τ_L=20 s, laser power 930 mW. Both figures (a) and (b) show the dark signal obtained under identical experimental conditions for comparison.

80%. For transitions from the lower subband the degree of spin orientation is equal to zero.[12] The splitting of the upper valence band for GaAs under uniaxial strain at 77 K increases roughly linearly with applied pressure and can amount up to several tenths of an eV at this temperature.[13] In our case, the applied pressure was low (21.6 MPa) and corresponds to a splitting of less than 0.01 eV. It is not anticipated that this value changes considerably upon lowering the temperature. The electronic spin orientation at the band gap should lead to a strongly enhanced NMR signal if interaction with conduction electrons were a dominant mechanism for polarizing the nuclei. Figure 3(a) shows that no further enhancement at the band gap was observed. If photoinduced conduction electrons are present during NMR data acquisition, a shift of the nuclear magnetic resonance frequency is expected in analogy to the Knight shift observed in metals. Sample irradiation during data acquisition did not lead to any shift of the NMR signal with respect to the Boltzmann equilibrium signal. Analogously, no Knight shift was observed in differently doped 3D GaAs crystals,[5] whereas in quantum wells, such a shift was observed and attributed to hyperfine interaction with photoexcited electrons in the conduction band.[1–3] Thus, interaction with conduction electrons does not seem to be the dominant mechanism of nuclear polarization in three-dimensional crystals.

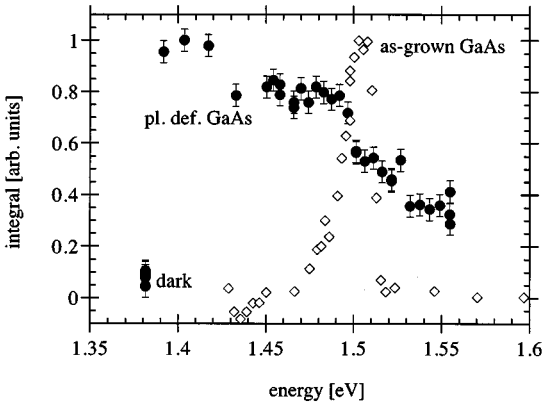

FIG. 3. Dependence of the integrated ^{69}Ga NMR signal intensity on the energy of the irradiation light for circularly polarized light at $T=2$ K. Single pulse excitation (pulse width 9 μs). Irradiation time $\tau_L=120$ s. Full dots, plastically deformed crystal; empty diamonds, as-grown GaAs. For the plastically deformed crystal, the dark signal intensity is indicated. For the as-grown crystal, no dark signal could be detected under the experimental conditions.

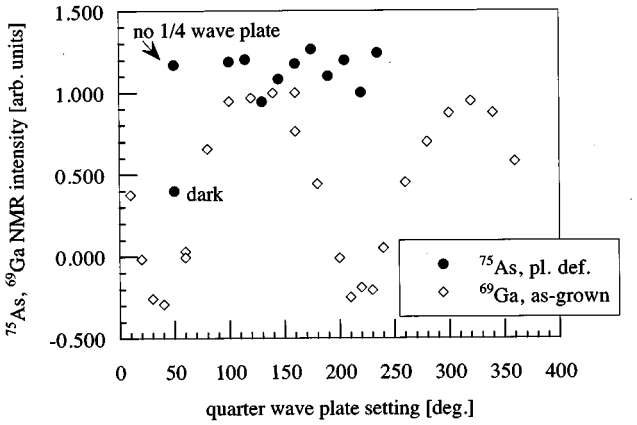

FIG. 4. ^{75}As NMR integrated signal intensity of plastically deformed GaAs in dependence of the helicity of the pumping light displayed as setting of the quarter wave plate in degrees. The spectrum was recorded with a quadrupolar echo sequence to avoid baseline distortions (pulse width 6 μs, interpulse delay 100 μs). Irradiation time $\tau_L=120$ s. $T=6$ K.

A phase inversion of the NMR signal gives evidence for optical pumping as the dominant enhancement mechanism.[5] In fact, inverting the electronic polarization by pumping with σ^+ or σ^- light results correspondingly in an inverted nuclear polarization.

In Fig. 4, the dependence of the ^{75}As NMR signal intensity on the polarization of the laser light is shown for the plastically deformed crystal (full circles) and the as-grown crystal (empty diamonds). In the latter case, the phase of the signal is inverted for opposing circular helicity (σ^+ or σ^-), while in the former case, no modulation of the signal intensity is observed for varying light polarization. Thus, optical pumping does not seem to be the dominant enhancement mechanism in the plastically deformed crystal. The same enhancement is observed when irradiating with linearly polarized light which equalizes the electron spin state population (Fig. 4). This supports the idea that an Overhauser effect is the dominant enhancement mechanism.[14,15] Efficient electronic recombination and relaxation mechanisms can prevent a phase inversion of the NMR signal.[5] In the case of the plastically deformed crystal, fast electronic relaxation due to the high density of defects may short-circuit the populations of the electronic Zeeman spin levels, thus quenching a possible optical pumping effect. A similar effect has been observed in heavily p-doped GaAs, where the high concentration of p dopants reduces the electronic recombination and relaxation times and thus prevents the phase inversion of the NMR signal.[5] A decreased nuclear spin-lattice relaxation time upon irradiation may also contribute to build up a Boltzmann nuclear polarization.

In conclusion, we have studied a plastically deformed GaAs crystal with optically enhanced NMR in high field. The mechanism responsible for NMR signal enhancement supports previous results obtained for a three-dimensional as-grown GaAs crystal. Contrary to the mechanism discussed for two-dimensional systems (quantum wells), where interaction with conduction electrons presents the dominant mechanism for NMR signal enhancement, conduction electrons do not seem to participate in the nuclear polarization process in uniaxially strained GaAs. No Knight shift was observed when the NMR signal was detected during irradiation. The defects introduced upon plastical deformation, most likely dislocations, serve as traps for the electrons and allow for polarization transfer through the hyperfine interaction (Overhauser effect). The number of these states has been largely increased in the plastically deformed crystal when compared to the small number of shallow traps in the as-grown material. Moreover, the intragap states in the deformed crystal present a continuum of states giving rise to an enhanced NMR signal over a wide energy range below the band gap. The presence of an enhanced NMR signal above the band gap may be due to a reduced nuclear spin-lattice relaxation time within the irradiation volume and subsequent spin diffusion. Signal enhancement was observed independent on the helicity of the pumping light. As in the case of heavily p-doped GaAs, an enhanced NMR signal was observed even under irradiation with linearly polarized light, although no net orientation of the conduction electrons can be achieved.

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