ELECTRONIC STRUCTURE OF N-V CENTERS AND TERAHERTZ SPECTROSCOPY OF DIAMOND

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ABSTRACT

We report an essentially complete characterization of energies and relaxation processes of the lowest seven electronic states of the N-V (nitrogen-vacancy) center in diamond using several different nonlinear laser spectroscopic techniques. We have also applied ultrafast optical techniques to measure dielectric properties of CVD and bulk diamond in the 0.3-1.6 THz range for the first time.

INTRODUCTION

The N-V center with zero phonon absorption at 637 nm is one of the simplest and most studied radiation-induced centers in nitrogen-containing diamond [1]. It was somewhat surprising therefore that Manson and co-workers [2] recently questioned earlier assignments of its electronic states. However, their viewpoint was fully substantiated by subsequent work of Redman et al. [3], who used a combination of EPR and nearly degenerate four-wave mixing spectroscopy to show directly that the ground state was a spin triplet rather than a singlet as suggested earlier by Loubser and Van Wyk [4]. Here we present new results of high resolution optical spectroscopy involving persistent hole-burning, stimulated photon echo and two-beam coupling observations which confirm and extend these findings. Persistent hole-burning was used to determine zero field splittings of the ground and excited triplet states due to spin-spin interactions. Echo techniques with femtosecond pulses revealed quantum beats at oscillation frequencies in agreement with the hole-burning results. These short pulse experiments also characterized fast relaxation processes of the center. Two-beam coupling with frequency-locked dye lasers was used to elucidate slow decay processes.

We have also measured real and imaginary parts of the dielectric tensor for diamond in the Terahertz (THz) frequency regime. Preliminary results reported here were obtained by a precise ultrashort pulse technique [5] applied to bulk single crystals and free-standing CVD polycrystalline films. Broadband bursts of Terahertz radiation were generated by ultrashort optical pulses on a low-temperature-grown GaAs photoconductive dipole antenna, then collimated and passed through the material under study to an identical dipole receiver gated with variable-delay, synchronized pulses from the same laser. CVD diamond crystallite sizes were very much smaller than a wavelength, so these measurements furnish accurate values of refractive index and loss tangent over a broad range of millimeter wavelengths when film thickness is known. These values are the same as would be measured for dielectric constant and conductivity in single crystal diamond films of equivalent density and composition.

EXPERIMENTAL

Sample preparation has been described elsewhere, in reference [3], and there it was shown in a direct manner that the ground state of the N-V center is a spin triplet. Still earlier, uniaxial stress studies [6] showed that the first parity-allowed optical transition is between a ground state of A and an orbitally excited state of E symmetry. Consequently, with the further result from [3] that a metastable state exists between ^{3}A and ^{3}E, the electronic energy level scheme of Fig. 1 is obtained for the center. All states shown are within the gap.

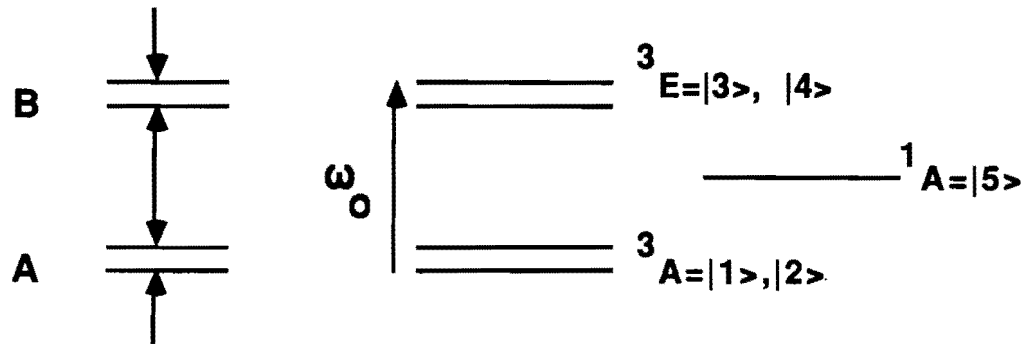

Figure 1. Energy levels of the N-V center in diamond.

Persistent Spectral Hole-Burning

Small spin splittings, such as the one labelled A in Fig.1 between singly and doubly degenerate sub-levels of a triplet orbital state (partly split in zero field by spin-spin interactions), can easily be measured by electron paramagnetic resonance if they occur in ground states. More generally however, both ground and excited state splittings can be measured using various forms of optical hole-burning spectroscopy, which records transmission versus frequency following narrowband laser excitation. Here we first present persistent hole-burning measurements of the splittings A and B depicted in Fig. 1 for the N-V center. We then compare them with quantum beat measurements and in later sub-sections consider relaxation dynamics of the center and Terahertz response.

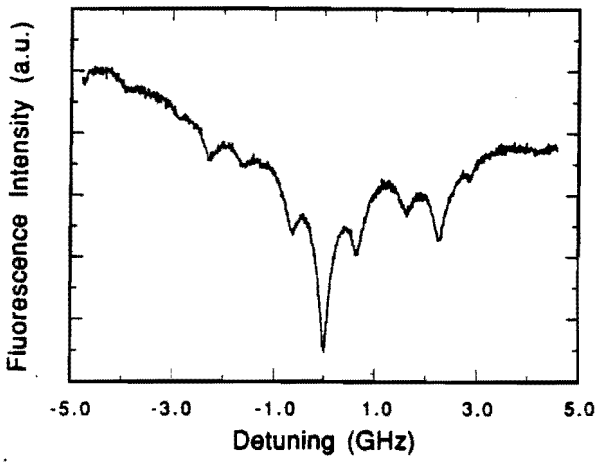

Figure 2. Persistent hole-burning spectrum of the N-V center at 637.87 nm at T=6.5 K.

Optical pumping among the ground and excited spin states of the N-V center was accomplished at liquid helium temperatures with radiation from a cw dye laser tuned to the zero phonon resonance at 637 nm. The re-distribution of population among homogeneous groups of N-V centers within the broad absorption linewidth (hole-burning) was observed by probing absorption changes induced by the pump laser on a fine frequency scale. In our experiments, we observed both transient and persistent changes in absorption in the detuning range 0-10 GHz. Below 70 K, it was possible to observe the spectrum of Fig. 2 after delays of up to an hour by tuning a weak probe beam through the spectral region of the "bleaching" laser. The extraordinary persistence of "satellite" features seen in this spectrum was previously unexplained [7], but all features can now be accounted for by assigning zero field triplet spin splittings of A=2.88 GHz and B=0.65 GHz. That is, all holes appear at frequency shifts of $\pm$A, $\pm$B, $\pm$(A-B), $\pm$(A+B), or $\pm$(A$\pm$2B). The value for A is in excellent agreement with ground state EPR [3,4], whereas B has not been measured previously.

Ultrafast Quantum Beat Spectroscopy

A direct, all-optical method of verifying splittings in the triplet manifolds and of measuring the values of A and B is to observe fluorescence or coherence decay following short pulse excitation. This method relies on preparation of a coherent superposition of the two ^3A and the two ^3E states, and observation of interference between dipole-allowed transitions in subsequent emission of the system. We used cavity-dumped 800 fs pulses from a two-jet, synchronously mode-locked DCM dye laser to excite the N-V center at 637 nm. Two counter-propagating pump pulses mixed with a weak probe pulse within the sample to generate an accumulated 3-pulse echo propagating opposite to the probe and exhibiting the dependence on delay shown in Fig. 3.

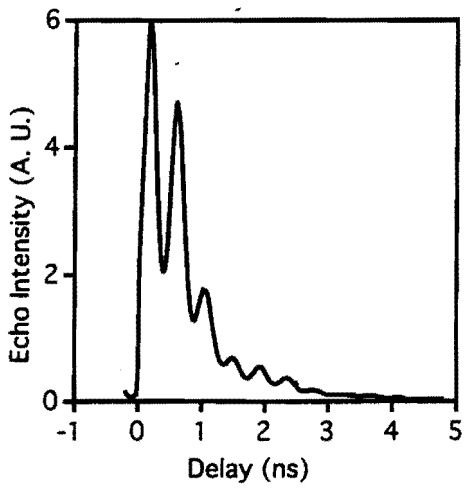

Figure 3. Three-pulse stimulated echo signal versus probe delay for λ=637 nm at T=6.5 K.

The observed oscillations for co-polarized beams occurred at a frequency of 2.2 GHz as determined by FFT analysis. This frequency is in excellent agreement with the difference frequency A-B of the two spin-allowed transitions between the ground and excited state manifolds expected from persistent hole-burning results. Here however, state splittings are implicated directly, without appeal to complex optical pumping and storage processes due to the ultrafast excitation mechanism. Interestingly, signals are also observed for cross-polarized forward pump and probe beams. These signals presumably originate from higher-order coherence among the sub-levels of each manifold. The temporal decay of the quantum beat envelope yields the dephasing time of the ^3E state directly. At 6.5 K this amounts to a few nanoseconds. The population decay time, obtained in separate measurements with delayed backward pump pulses, is 13.3 ns. These are the fast relaxation processes of the N-V center.

Two-beam coupling

Slow decay processes are ordinarily measured by fluorescence or phosphorescence decay experiments. However, if the decay is non-radiative or the wavelength of emission is unknown, frequency-domain techniques like four-wave mixing or two-beam coupling can be very useful.

In Fig. 4 the gain spectrum for a probe wave passing through a bulk single crystal of diamond containing N-V centers illuminated by a strong pump wave is shown. The two beams cross at a small angle in the sample, and spectral variations in the energy transfer between the two beams are well-known to depend sensitively on decay times of internal population dynamics of the center under study [8]. Since the basic relaxation processes within the N-V center have been described previously [3], we can compare the results of two-beam coupling quantitatively with earlier work.

We find that two exponential decay processes are required to describe the observations in Fig. 4. The two-beam coupling spectrum itself is therefore a superposition of in-phase and out-of-phase components of two contributions from distinct dynamical processes. The fitting parameters consist of the corresponding relaxation times t_1 and t_2, and real and imaginary parts of the nonlinear refractive index n_2. The solid curve in the figure is a least squares fit to room temperature data with $t_1 = 50 \pm 2$ ms, $t_2 = 0.64 \pm .01$ ms, and $n_2''/n_2' = -1.01 \pm .04$. For comparison with earlier determinations by four-wave mixing (NDFWM), two-beam coupling was also performed at 77 K with the result that $t_1 = 92 \pm 30$ ms, $t_2 = 1.1 \pm .1$ ms, and and $n''/n_2' = -0.9 \pm .1$. Excellent agreement is obtained for t_2 when compared to the precise NDFWM determination $t_2 = 1.170 \pm .003$ ms, whereas t_1 is somewhat shorter than the NDFWM value $265.3 \pm .6$ ms. However t_1 from beam coupling does approach the NDFWM value as intensity and chopping duty cycle are reduced. This indicates that the qualitative description of the diamond beam coupling spectrum is excellent and the quantitative comparison with earlier results satisfactory. On this basis the two components t_1 and t_2 in the beam coupling spectrum may be identified as arising from intersystem crossing ($^1A \rightarrow {}^3A$) and spin-lattice relaxation ($^3A(b) \rightarrow {}^3A(a)$) respectively.

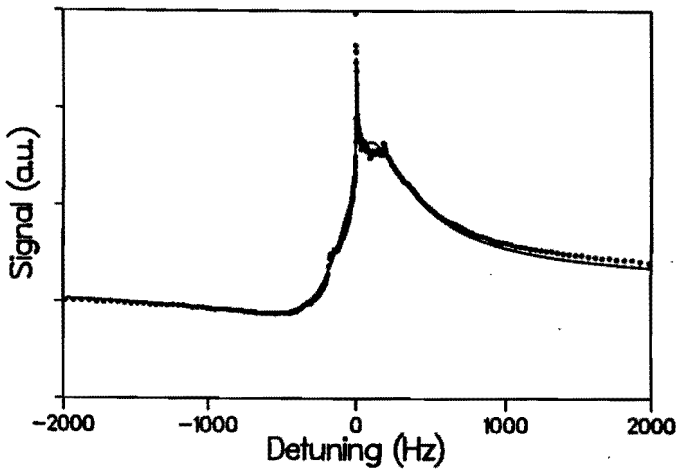

Figure 4. Two-beam coupling signal versus pump-probe detuning. The solid line is a least squares regression based on two-component nonlinear response.

Terahertz spectroscopy

Single cycles of Terahertz radiation of approximately 600 fs duration were generated by 100 fs optical pulses incident on photoconductive antenna structures integrated on GaAs wafers. Collimation was accomplished using a hyper-hemispherical Silicon lens constructed of high resistivity material. Detection relied on a similar arrangement in which the receiver voltage was sampled with 100 femtosecond timing accuracy using optical pulses derived from the same laser. In Fig. 5 the real and imaginary parts of the dielectric constant determined in this way are presented for two nominally undoped, free-standing diamond films of area 1 cm^2 and thicknesses 20 and 60 μm grown by filament-assisted chemical vapor deposition (FACVD).

When losses are dominated by free carrier absorption, the variations in the imaginary index reflect changes in the bulk conductivity versus frequency. Thus, given accurate determinations of film thickness, data such as that in the lower curve of Fig. 5(b) provide an elegant method for characterization of millimeter wave conductivity over a very wide band.

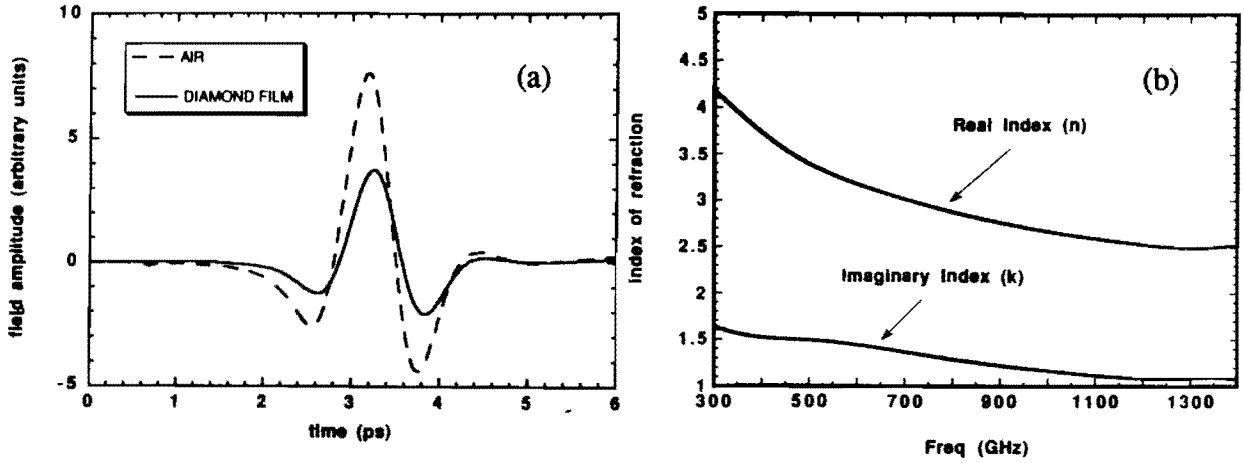

Figure 5. (a) Detected Terahertz pulsed field strengths versus time, with and without a free-standing FACVD diamond film (estimated 20 μm thickness) placed between transmitter and receiver. (b) Refractive index and conductivity of the diamond film derived by preliminary analysis of pulse envelope modulation and phase delay.

The rapid rise in the real index toward lower frequencies evident in Fig.5 is incompletely understood at this time, but is probably due to low frequency electromagnetic resonances associated with dangling bond and impurity spin excitations. Systematic measurements are in progress to correlate these parameters with film morphology, doping and growth conditions as well as to make direct, quantitative comparisons with bulk single crystals.

SUMMARY

Determinations of the electronic structure and dynamics of the lowest seven states of the N-V center in diamond constitute the main results of this work. We have made high resolution observations of the splitting of doubly degenerate and singly degenerate spin states associated with the orbital singlet ground state and the lower component of the orbital doublet excited state, in zero field. Results obtained by persistent hole-burning agree well with those from quantum beat spectroscopy. Evidence [3] for the existence and relaxation rate of a postulated intermediate ^1A state has not been discussed here, but completes our picture of lowest-lying energy states of the center.

Fast population decay, optical dephasing and slow dynamics due to intersystem crossing and spin-lattice relaxation have also been studied. The decay constants associated with each state were determined accurately with a combination of photon echo and beam coupling techniques. Overall, our measurements constitute a rather complete picture of the electronic structure and fundamental relaxation processes of the N-V center. Finally we have presented preliminary measurements of dielectric properties of CVD diamond at Terahertz frequencies using all-optical techniques easily extendable to other widegap semiconductor thin films.

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