1994

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Abstract

Thin film synthetic diamond promises to be the next semiconductor material, if the manufacturing processes which produce it can be controlled. Solid state nuclear magnetic resonance (NMR) using magic angle spinning (MAS) is used to measure the content of hydrogen in diamond which controls the resistivity of the diamond thin films. Spectral results are presented for proton NMR of thin film synthetic diamond. Experimental calibration techniques using BaF_2 as the hydrogen standard will be discussed, as well as acquisition times, pulsing sequences, spinning rates, and rotor composition.

Introduction

Solid State Effects.--In a magnetic field, atomic nuclei which poses a magnetic moment will interact with the magnetic component of r.f. irradiation, elucidating information about nuclear spin interactions, Such interactions, in turn, yield information about the composition and structure of the sample. For a spin 1/2 nucleus such as ^1H, in a uniform field, these interactions can be described by the total Hamiltonian (K.M. McNamara and K.K. Gleaason, 1992):

$$H_{tot}=H_z+H_{d,ii}+H_{d,is}+H_{cs,is}+H_{rf(t)}+R(t) \qquad (1)$$

where H_z is the Zeeman interaction between the observed nucleus and the external magnetic field; $H_{d,ii}$ is the interaction between the observed nucleus and the magnetic field generated by neighboring nuclei of the same species (homonuclear dipolar coupling); $H_{d,is}$ the interaction between the observed nucleus and the magnetic field generated by neighboring nuclei of the different species (heteronuclear dipolar coupling); $H_{cs,is}$ the interaction between the observed nucleus and nearby bonding electrons (chemical shift interaction); $H_{rf(t)}$ is the experimentally controlled Hamiltonian produced by the magnetic component of r.f. irradiation; and $R(t)$ is the coupling of observed nuclei to fluctuating magnetic fields in the lattice, primarily a result of phonon (thermal) modes or due to paramagnetic centers. This last component represents the process by which the spin system comes to equilibrium with the external field and is known as spin-lattice relaxation.

The Zeeman interaction is the dominant term in the total Hamiltonian, and the other terms are treated as perturbations on the Zeeman term. The effects of this term can be eliminated from (1) by changing the reference frame to one rotating at the resonant frequency of the observed nucleus. In addition, manipulation of $H_{rf(t)}$ allows selective suppression of the remaining Hamiltonians, simplifying the interpretation of the resulting spectra.

The homonuclear and heteronuclear dipolar couplings, $H_{d,ii}$ and $H_{d,is}$ between NMR active nuclei are responsible for a significant portion of the line broadening observed in the NMR spectra of solids. For diamond films with low hydrogen concentrations, the homonuclear coupling term $H_{d,ii}$ is small, and only the hetertonuclear term will be important. The dipolar coupling between ^1H nuclei is a strong function of internuclear spacing and depends on the angle between the internuclear vector and the direction of the applied magnetic field. The dipolar decoupling term, D, (Komoroski, 1986) of the Hamiltonian $H_{d,is}$ may be expressed as:

$$D=h\gamma_c\gamma_H(3\cos^2\theta-1)/2\pi r^3 \qquad (2)$$

where γ_c and γ_H are the carbon and proton gyromagnetic ratios which are proportional to the magnetic moments of the nuclei; θ is the angle that the C-H vector makes with the external field; h is Plank's constant; and r is the distance between the nuclei. From this formula, it is seen

that the heteronuclear dipolar decoupling term is a strong function of internuclear distances. The polycrystalline nature of diamond films produces C-H vectors of all possible orientations, and their individual contributions inhomogeneously broaden the normal spectra toward a Gaussian shape. In solutions, the effects of dipolar coupling are removed by very rapid rotational and transnational motions which average the angle dependent term to zero. Weak dipolar decoupling interactions of a solid sample may be reduced by mechanically spinning the sample at 54.74°, which is known as the magic angle. Rotation at this angle at speeds greater than the dipolar linewidth, called magic angle spinning (MAS) (Komoroski, 1986), reduces the $3\cos^2\theta-1$ term to zero.

The chemical shift interaction, $H_{cs,is}$ arises from the surrounding electrons which shield the nuclei from the external magnetic field. The chemical shift is directionally dependent, as the electronic shielding varies in a molecule. Once again, rapid molecular reorientation in liquids reduces these contributions of the anisotropic chemical shift to an isotopic average. For solids, the chemical shift anisotropy (CSA) will cause individual peaks to overlap and can reduce the spectrum to a featureless mound. MAS at or above half the width of the CSA pattern will reduce the anisotropy to its isotopic average, but also produces rotationally dependent sidebands which appear about the central peak at distances equal to the spinning speed.

Materials and Methods

Sample Preparation.--Two 600 mg samples of diamond film labeled TD 1114 and TD 1117 were obtained from Norton Diamond Films. The samples were gently broken with an agate mortar and pestle so that they would fit into the 9.5 mm sample rotor. The NMR used for the experiments is a GE GN300 with a Chemagnetics CMP 300 VTH solid state probe with MAS capability. A Chemagnetics Kel-F rotor was used to spin the sample within the probe assembly. The Kel-F (polychlorotrifluoroethylene) rotor produces little NMR signal due to its large dipolar coupling which broadens the signal beyond high-resolution detection (Komoroski, 1986).

Before the samples could be used in an experiment, background hydrogen signals from airborne water vapor and contamination of the probe surfaces due to handling must be removed. The rotor and the samples were cleaned and soaked in a 120°C oven for 18 hours prior to the experiments to drive off any physi-sorbed water in them.

A simple one pulse experiment with a 5-second delay between signal averages was used to obtain proton spectra for the rotor only, for the rotor and the barium fluo-

ride packing material, and for the rotor will barium fluoride packed around the TD1117 diamond film slivers. Additionally, the drive pressure of the MAS unit was varied to produce a static spectrum and spectra at two different speeds. The barium fluoride packing material was chosen due to its low proton content. Levy and Gleason (1993) extrapolated that a 0.45 g sample of barium fluoride contains ~3.5 X 10^{16} hydrogen atoms, which is the lowest published hydrogen detection level from a solids NMR experiment. The probe ninety degree pulse width was determined with a quadropolar doped (Cu_2SO_4) water sample in a peak inversion experiment. The experiment was allowed to run 4096 scans.

Results and Discussion

The TD1117 sample was chosen for the experiment because the included analysis indicated that it possessed the largest percentage of impurities (including hydrogen), and thus, a proton spectra could more easily be obtained (Beera, 1993). The rotor only experiment showed a flat response when scaled to the same intensity scale as the rest of the experiments. Similarly, the barium fluoride spectrum Fig. 1 indicated several unresolved Gaussian shaped peaks at from 0-2000 Hz. The static TD1117 diamond in the BaF_2 experiment (Fig. 2), shows a Lorentzian peak with a Gaussian base. This is expected for a static sample since the dipolar coupling and CSA broadening effects are present. Half-width at half-height measurements indicate a line width of 6000 Hz. MAS results for the TD1117 diamond film (Fig. 3 and 4), show a marked decrease in the line width to 35 Hz. Also present in the spectra are spinning sidebands from the CSA frequency mixing. In Fig. 3, three sets of spinning sidebands are evident; the sidebands at 3050 Hz and -1900 Hz are due to first order frequency mixing and indicate a spinning speed of 2500 Hz. The sidebands which occur within the primary sidebands are due to frequency folding because of the limited spectral width (10000 Hz) of the experiment. The spectrum in Fig. 4 shows only the primary Lorentzian peak with a small Gaussian component. The sidebands are evident at 3708 Hz and -2493 Hz which suggest a MAS speed of 3089 Hz. Also evident in theses spectra are the BaF_2 undifferentiated peak at 1500 Hz and perhaps a secondary peak downfield from the main 587 Hz diamond peak at 480 Hz. The relative height of the central diamond peak to the barium fluoride peak indicates that the diamond sample has many times more hydrogen than the barium fluoride sample. Future experiments will quantify the barium fluoride hydrogen, as well as the diamond hydrogen for the various chemical environments of the hydrogen in the samples.
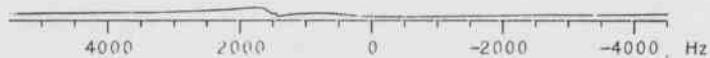
Fig. 1. MAS proton spectra of barium fluoride. A small Gaussian peak extends from 2000-0 Hz, with an unresolved Lorentzian component at 1500 Hz. Intensity on all graphs is the same.
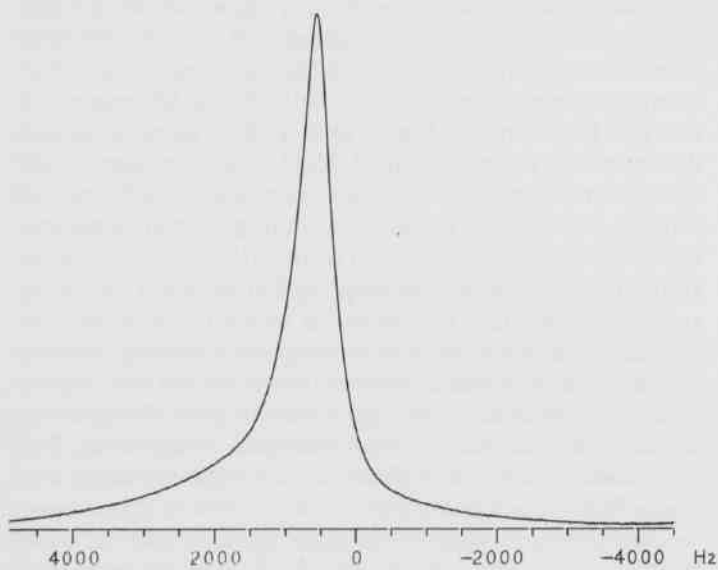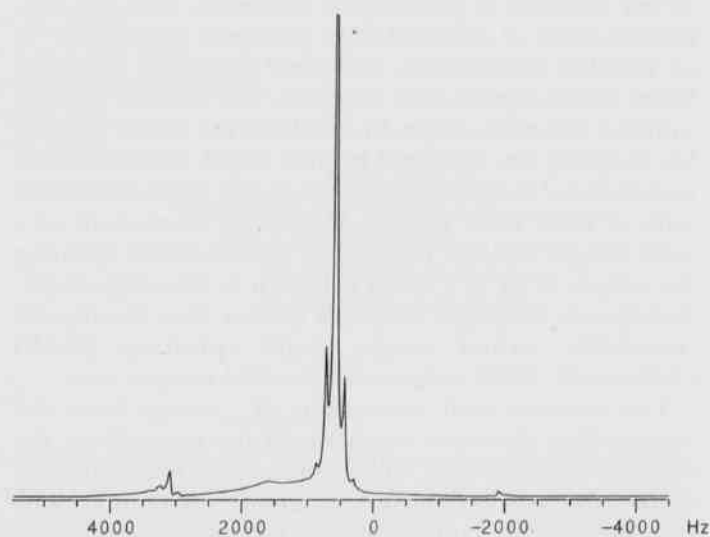

Fig. 3. MAS proton spectrum of TD1117 diamond film. Symmetrical peaks around larger central diamond peak are from spinning sidebands. The smaller peaks within the primary sidebands at 3750 and -2500 Hz are due to spectral width induced frequency folding. Primary sidebands indicate a MAS spinning speed of -2600 Hz. The small barium fluoride peak is evident at 1700 Hz.

Fig. 2. Static proton NMR spectrum of TD1117 synthetic diamond thin film. The spectrum is broad due to the anisotropic effects of dipolar coupling and chemical shift anisotropy.
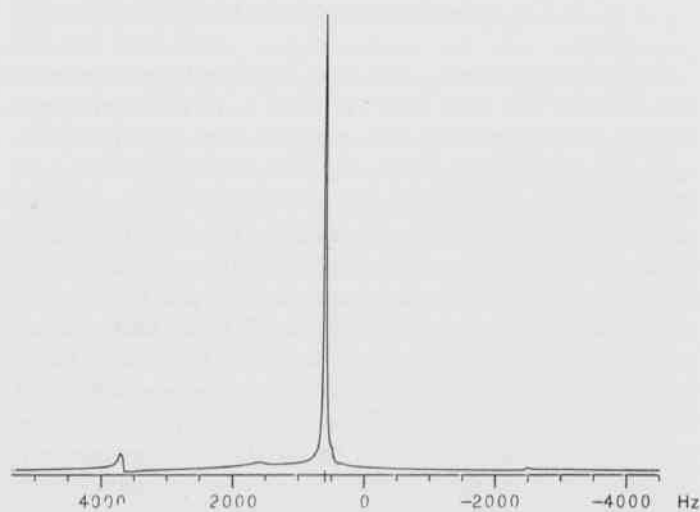

Fig. 4. MAS proton spectrum of TD1117 diamond film. Primary sidebands indicate a MAS spinning speed of ~3080 Hz. The small barium fluoride peak is again evident at 1700 Hz. A small peak on the right shoulder of the central peak can be seen possible indicating a secondary proton environment.

Literature Cited

Beera, R.A. 1993. Characterization of Diamond Samples, Internal Document.

Komorowski, R.A. 1986. High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk, VCH, 16-61.

Levy, D.H. and K.K. Gleason. 1993. Nuclear Magnetic Resonance Probe for Low Level Hydrogen Detection, J. Vac. Sci. Technol., Vol 11(1): 195-198.

McNamar, K.M. and K.K. Gleason. 1992. Selectively ^{13}C-Enriched Diamond Films Studied by Nuclear Magnetic Resonance, J. Appl. Phys., 71(6): 2884-2889.