Direct Determination of Carbon Hybridization in Amorphous Carbon Films using ^{13}C N.M.R. Spectroscopy

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The concentration of sp^2 and sp^3 carbon atoms in an amorphous carbon film has been determined directly from ^{13}C n.m.r. spectroscopy, which also shows that the majority of the hydrogen atoms are attached to sp^3 carbon atoms.

The growing success of amorphous silicon[1] in device applications points to research into other fields of amorphous materials. A fundamental requirement in the preparation of these materials for electronic applications is control of the co-ordination number and bonding of the constituent atoms since these will have a profound influence on the materials' optical and electronic properties. Unlike amorphous silicon, which contains only sp^3 Si atoms in a disordered network, amorphous carbon contains sp^3 and sp^2 hybridized atoms because of the presence of single and double bonds. Given the wide range of optical and electrical properties displayed by amorphous carbon films and the different structural models presented to describe them,[2,3] the accurate determination of the partitioning of the atoms between the two co-ordination types is essential in developing a complete understanding of the amorphous carbon system.

In this paper we show that the use of high-resolution ^{13}C n.m.r. spectroscopy provides a direct determination of the concentrations of sp^2 and sp^3 carbon without resort to involved theory. The experiment also provides information about the bonding of hydrogen atoms (always present in materials prepared by the plasma technique) to the two carbon types.

An amorphous carbon film was prepared from a r.f. glow-discharge in methane gas maintained at a pressure of 0.26 Pa in a stainless-steel vacuum chamber. A glass substrate was attached to the powered electrode (cathode) which was biased to −350 V by capacitive coupling to the r.f. power supply operating at a frequency of 13.56 MHz. After a deposition of 8 h the substrate was removed from the chamber. The optical gap of the material was estimated to be 1.1 eV from a Tauc plot[4] using the transmission spectrum, obtained in the range 400—1500 nm, and the film thickness of 10 μm. The hydrogen to carbon ratio in the material was determined from chemical analysis to be 1.38 : 1. The material was highly insulating, having a room temperature resistivity of $>10^8$ Ω cm. These values are typical for carbon films grown by plasma techniques.[5,6]

For n.m.r. measurements, the film was removed from the substrate, mixed with finely ground KBr, and loaded into a high-frequency sample spinner made of polychlorofluoroethylene (Kel F). Cross-polarization (c.p.) ^{13}C n.m.r. spectra were obtained at 15.1 MHz on a JEOL FX-60 spectrometer operating at 1.41 T using a magic-angle spinning probe. The corresponding ^1H frequency was 60 MHz. A single c.p. contact time of 2 ms was used with a delay of 0.5 s, and 400 000 transients were collected over a 56 h period. The transformed spectrum is shown in Figure 1(a). Two broad peaks, at 136 and 45 p.p.m. *vs.* Me_4Si, are clearly resolved, which are in the ranges established for sp^2 and sp^3 carbon respectively. The integrated peak intensities for the sp^2 and sp^3 regions are 55 and 45% respectively. In view of the very long data accumulation times, owing to the small sample size (~30 mg), the c.p. conditions were not optimized but were assumed to be the same as those appropriate for obtaining quantitative spectra on coal samples. Unless significant portions of the sample contain carbon atoms some distance removed from hydrogen atoms, unlikely in view of the high hydrogen content, we may assume that the spectrum is closely quantitative. In general, c.p. rates for sp^2 carbon are lower than for sp^3 carbon suggesting that, if the c.p. contact time is not optimal in the work, then the figure for 55% sp^2 carbon represents an under-estimation of the true concentration. The value is somewhat larger than the concentrations for sp^2 carbon obtained by electron energy loss[5] and i.r. spectroscopy[7] of materials prepared using different hydrocarbon precursors and different growth conditions.

The n.m.r. technique also permits a determination of the partitioning of hydrogen atoms between the two carbon environments. By switching off the proton spin-lock pulse for a short time prior to data acquisition, the carbon atoms directly bonded to hydrogen dephase and are reduced in intensity in the resulting ^{13}C n.m.r. spectrum. Using a dephasing time of 40 μs results in a two-fold greater reduction

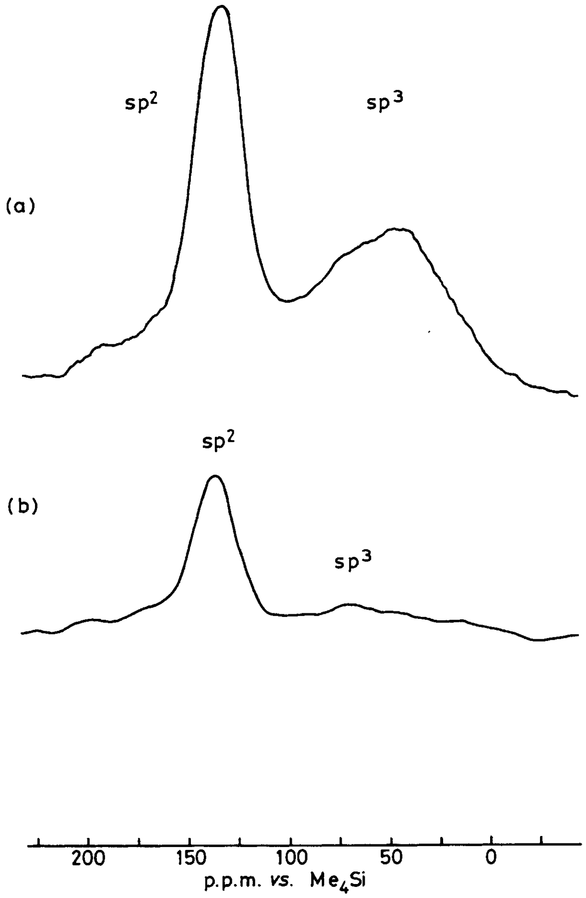

Figure 1. ^{13}C N.m.r. spectra of amorphous carbon obtained using cross-polarization and magic-angle spinning: (a), single contact time of 2 ms; (b), contact time of 2 ms plus dephasing time of 40 μs.

in intensity of the sp^3 region compared to the sp^2 region, as shown in Figure 1(b). This indicates that a larger proportion of the hydrogen is bound to sp^3 than to sp^2 carbon. This result is not unexpected on purely statistical grounds since a maximum of 1 bond for sp^2 and 2 bonds for sp^3 are available for hydrogen attachment after formation of a contiguous network. This method provides information complementary to i.r. spectroscopy in that the latter, because of wide variations in oscillator strengths for the different C–H vibrations, is better suited to identifying the presence of particular structural features.

We have demonstrated that high-resolution ^{13}C n.m.r. spectroscopy provides direct information about both the hybridization of carbon atoms in amorphous carbon thin films, and the partitioning of the hydrogen atoms in the sample between the two possible carbon types. The value of 55% for the proportion of sp^2 carbon atoms shows that the structure of plasma-deposited amorphous carbon is clearly different from that of materials prepared by evaporation or pyrolysis techniques which appear to contain a much higher proportion of sp^2 carbon atoms.[8] We are proceeding to investigate how these parameters influence the optical and electrical properties of amorphous carbon, which can be varied over wide ranges depending upon the deposition conditions used.

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