A Variable temperature X- and W-band EPR study of SiCN/Fe ceramics

Sergey. I. Andronenko[1], A. Rodionov[1], Sushil K. Misra[2]
[1]Institute of Physics, Kazan Federal University, Kazan, Russian Federation, 420008
[2]Department of Physics, Concordia University, Montreal, Qc, H3G 1M8, Canada
E-mail: sergey.andronenko@gmail.com

Introduction

SiCN is a new class of materials for high-temperature electronics. Magnetic properties of SiCN materials doped with different transition metal ions can vary from paramagnetic to superparamagnetic and to ferromagnetic. Superparamagnetic materials are potentially useful in developing high-temperature magnetic-sensor devices. Magnetic composites, as well as electrically conductive ceramics, with properties varying from dielectric to semiconductor, can be easily produced using liquid silazane polymer as a base, and exploited to fabricate complex isolator-conductive-material structures in order to develop new MEMS-SiCN techniques [1]. Consequently, investigation of SiCN ceramics and its conductive and magnetic derivatives is currently of great interest. Further, sp^2 and sp^3-carbon related dangling bonds, which are usually formed in free carbon phase of SiCN [2] can be investigated by EPR, a powerful technique to detect various types of magnetic properties. It has turned out to be very effective in the study of such materials [3].

EPR study of SiCN/Fe ceramics

Polymer-derived SiCN ceramics, annealed at 1000° C, 1100° C, 1285° C, and doped with iron (III) acetylacetonate, were investigated at liquid-helium temperatures from 4 to 120 K. The X-band (9.425 GHz) EPR spectra are shown in Fig. 1. The broad EPR lines A and B belong to different Fe-containing crystalline phase with different temperature behaviour.

EPR study of dangling bonds

The narrow EPR line near g = 2.00 is due to two carbon related dangling bonds. It is without structure at X-band, but at W-band this structure becomes resolved. These two types of carbon-related dangling bonds are present (i) on the surface of the free-carbon phase (sp^2-carbon related dangling bonds) as defects, and (ii) within the bulk carbon phase (as sp^3-carbon related dangling bonds).

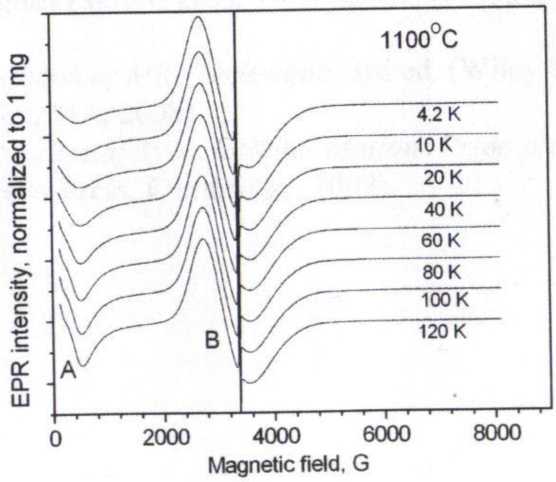

Figure 1. Temperature variation of EPR spectra of SiCN ceramic annealed at 1100° C at X-band

Temperature dependence of EPR linewidth of dangling bonds

The EPR linewidth of dangling bonds is strongly temperature dependent as shown in Fig. 2. The temperature dependence of EPR linewidth in the liquid-helium temperature range was found to be well described by the exchange interaction (J) in amorphous materials between carbon dangling bonds as deduced by Misra [4]. Accordingly, $\Delta B = A' + B' * T + C' / \left(1 + \exp\left(\frac{J}{T}\right)\right)$. In this expression, A′, B′, C′ are constants and T is the temperature. The second and third terms represent the relaxation of an exchange-coupled pair of spins in an amorphous solid. It was found by fitting the data that the value of the antiferromagnetic interaction was rather high (~ –80 K) in the various SiCN ceramic samples investigated here.

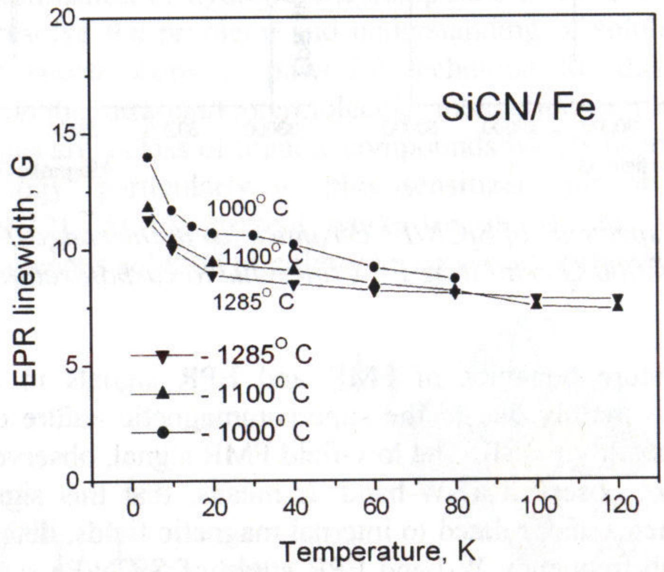

Figure 2. Temperature dependence of X-band EPR linewidth of dangling bonds for three samples annealed at 1285°, 1100°, and 1000°C

EPR/FMR study of SiCN/Fe ceramics: Fe-containing crystalline phase

The two FMR lines A and B in Fig. 1 are due to Fe ions, with different magnetic characteristics. They exhibit different temperature behavior. It is possible to use the temperature dependence of integrated FMR absorption linewidth to determine the Curie temperatures. This, in turn, can be used to determine the chemical composition of Fe-containing crystalline phase.

Critical temperature as determined from the FMR line A

As the temperature was increased from 290 K, the area under this absorption line, as obtained by double-integration of the first-derivative absorption curve, decreased and approached zero at 400 K. This integrated intensity is proportional to the magnetization of the ferromagnetic particles of Fe_5Si_3 in the sample.

The FMR linewidth of line A was fitted to the following expression [5] exhibiting the temperature (T) dependence:

$$\Delta B = \Delta B_0 + A|T_c - T|^{-0.7} \quad (2)$$

The best fit yields the values: $\Delta B_0 = (220 \pm 10)$ G, $A = (5.2 \pm 0.5)\times 10^3$ G $\cdot K^{0.7}$, and $T_C = (393 \pm 5)$ K. This Curie temperature is very close to that for Fe_5Si_3 ($T_C = 393$ K).

W-band EPR study

The EPR study of SiCN ceramics, annealed at 1100° C was carried out at 300 K at W-band (93.96 GHz). EPR signals due to Fe ions were observed. The two well resolved sharp EPR lines at ~33,000 G are due to sp^2- and sp^3 – carbon-related dangling bonds.

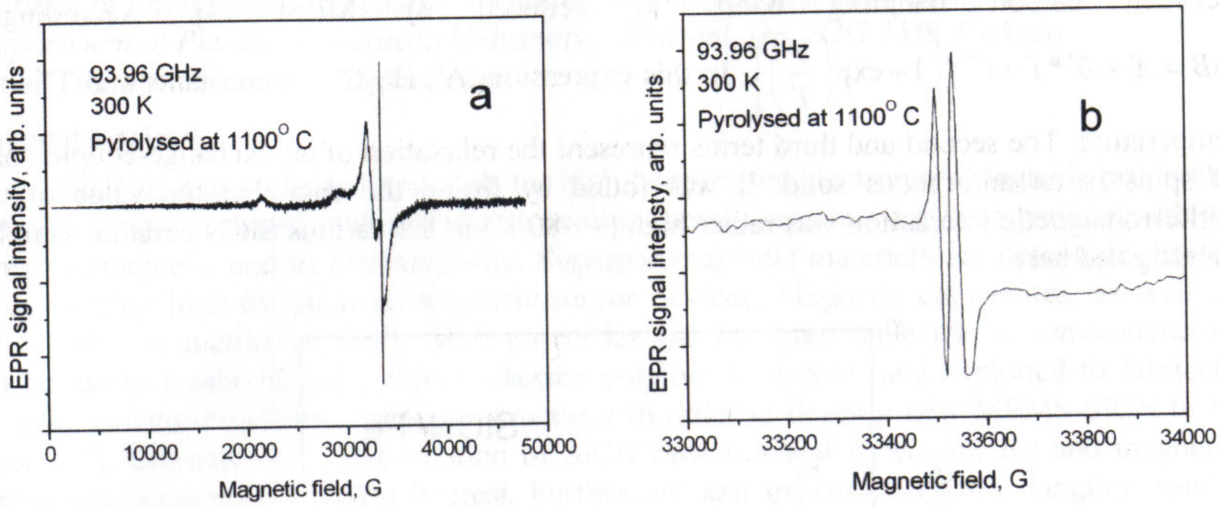

Figure 3. W-band EPR spectrum of SiCN/Fe ceramics (a) in the range 0-48,000 G and (b) in the range 33,000 – 34,000 G exhibiting EPR lines due to carbon-related dangling bonds

Conclusions

The low-temperature behavior of FMR and EPR signals in SiCN nanoparticles, activated with Fe ions is mainly due to the superparamagnetic nature of nanograins of Fe-containing compounds, mainly Fe_5Si_3. The low-field FMR signal, observed in SiCN/Fe near g = 10.0 at X-band, is not observed at W-band. It means, that this signal is not related to localized magnetic moments and, related to internal magnetic fields, determined by collective magnetic moments. High-frequency W-band EPR study of SiCN/Fe samples clearly shows, that central broad EMR lines observed at X-band are split into two different lines at W-band.

The two observed W-band EPR lines are due to carbon-related sp^2 and sp^3-dangling bonds. They are: (a) those associated with the aromatic rings of graphene layers with the g-value 2.0011 and (b) those existing in the bulk of "free" carbon phase with g = 2.0033 The EPR line with g = 2. 0033 is associated with sp^3-carbon related dangling bonds in amorphous carbon and the EPR line with g = 2.0011 is associated with sp^2-carbon related dangling bonds, which are located in broken aromatic rings of graphene layers.

Acknowledgements

This research was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) (SKM); SIA is grateful to Ministry of Education of Russian Federation, for partial support in the frame of research project, allocated to Kazan Federal University. SIA is grateful to Dr. S.B. Orlinskii for high-frequency measurements.

References

1. A. Leo, S. Andronenko, I. Stiharu, R. B. Bhat. – *Sensors*, **10**, 1338-1354 (2010).
2. S.I. Andronenko, I. Stiharu, S.K Misra. – *J. Appl. Phys.*, **99**, 113907 (2006).
3. S.I. Andronenko, I. Stiharu, S.K. Misra, C. Lacroix, D. Menard. – *Appl. Magn. Res.*, **38**, 385-402 (2010).
4. S.K. Misra. –*Phys. Rev.B.*, **58**, 14971-14977 (1998).
5. L.D. Landay, E. M. Lifshitz. Course of Theoretical Physics, v.5.: Statistical Physics. 4th ed. –"Nauka", Moscow, 1995; "Butterworth", London, 1999.