Point defects in hexagonal boron nitride. III. EPR in electron-irradiated BN

E. Y. Andrei, A. Katzir, and J. T. Suss
Solid State Physics Department, Soreq Nuclear Research Center, Yavne, Israel
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A new paramagnetic center was produced by 550-kV electrons in hexagonal boron nitride. It is shown that this center is a three-boron center and consists of an electron trapped in a nitrogen-ion vacancy (F center). The hyperfine interaction was found to be anisotropic with $A_\perp = 40.0 \pm 0.5$ G and $A_\parallel = 45.3 \pm 0.5$ G for the interaction with ^{11}B nuclei. The g factor was found to be $g = 2.0020 \pm 0.0008$. The thermal stability of this center was investigated.

INTRODUCTION

Defects associated with nitrogen vacancies, impurities, and trapped charges in hexagonal boron nitride (BN) were subjected to a theoretical and experimental study, discussed in Papers I and II of this work.[1,2] Most of the research efforts in the past were concentrated on a paramagnetic center which was shown to be a trapped electron interacting with three neighboring boron nuclei.[3] It was also shown[4] that the condition for the existence of this center is the presence of carbon as an impurity in BN. The model proposed[1,2] for this carbon-associated three-boron center is that of an electron trapped in a nitrogen-ion vacancy (F-center-type defect). We report here a new paramagnetic center which can be produced by electron irradiation in both "carbon-free" and carbon-containing hexagonal BN.

EXPERIMENTAL METHODS

Three types of hexagonal BN were used in this study: hot-pressed BN, pyrolytic BN, and compression-annealed pyrolytic BN. "Grade HP" hot-pressed BN was purchased from the Carborundum Co., and contained less than 0.05% carbon. "Boralloy" pyrolytic BN plates were purchased from the Union Carbide Corp., with a total impurity content of less than 10 ppm. Compression-annealed pyrolytic BN was prepared and kindly supplied to us by Moore and Singer.[4] All the above three types of BN consist of small crystallites, which are partially ordered with respect to a preferential c axis. In compression-annealed BN this ordering is so high that these samples resemble a single crystal. The samples used in this study were in the form of small plates (approximately $1 \times 3 \times 17$ mm), having their c axis perpendicular to the plane of the plates.

A commercial electron accelerator made by High Voltage Engineering Corp. was used for irradiation of the samples. All irradiations in this study were carried out at a voltage of 550 kV, and a current of 20 mA. The irradiation dose was varied by varying the irradiation time. During irradiation the samples were attached to a water-cooled copper sample holder, which kept the samples at room temperature.

A Varian EC-365 X-band electron-paramagnetic resonance (EPR) spectrometer was used. A special Lucite sample holder made it possible to vary the angle θ between the external magnetic field H_{dc} and the c axis of the samples.

RESULTS

The carbon-associated three-boron centers can be produced in hot-pressed BN and in compression-annealed pyrolytic BN by ionizing radiation (uv, x rays, or γ rays).[1] Such centers did not give rise to a detectable EPR signal in pyrolytic BN which was exposed to ionizing radiation or to electrons. Electron irradiation of hexagonal BN produces a new three-boron center. This new center was observed after electron irradiation in the above carbon-containing samples (hot pressed and compression annealed) as well as in pure pyrolytic BN. A typical EPR spectrum in compression-annealed pyrolytic BN that was electron irradiated for 16 h is shown in the upper part (I) of Fig. 1. Trace a represents a superposition of the new electron irradiation-produced three-boron center and the carbon-associated three-boron center. The latter appears in the central part of this trace as a single wide line, and is resolved in trace b using reduced gain and reduced modulation. The angular dependence of the hyperfine splitting A and of the g factor were measured. The sample was rotated about an axis in the plane of the BN hexagons (perpendicular to the c axis), thus varying the angle θ between the c axis and the external magnetic field

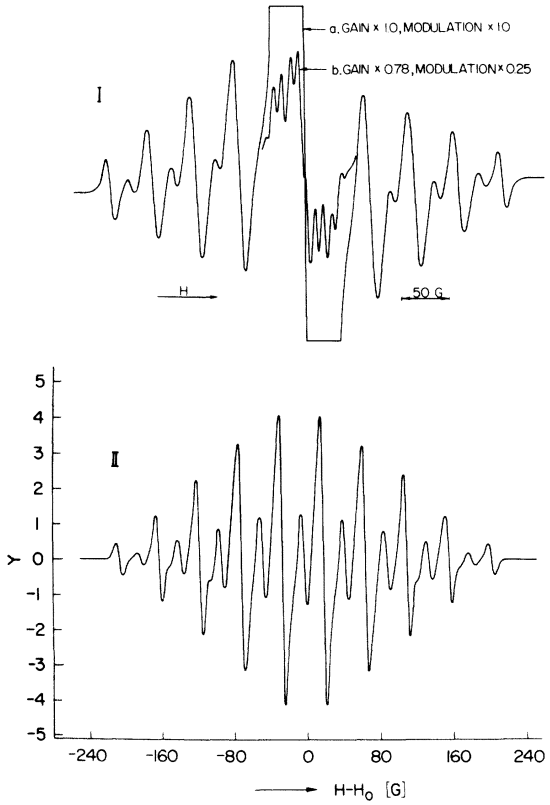

FIG. 1. (I) EPR spectrum of electron–irradiated compression-annealed pyrolytic BN, recorded at room temperature, with the external magnetic field H_{dc} along the c axis. (II) Computer simulation of an EPR spectrum of an electron interacting with three boron nuclei.

H_{dc}. The angular dependence of the hyperfine splitting $A(\theta)$ was found to fit the expression

$$A(\theta) = A_{\perp} + (A_{\parallel} - A_{\perp}) \cos^2\theta \qquad (1)$$

and is shown in Fig. 2. The computed best-fit values for $A_{\parallel}$ and $A_{\perp}$ are given in Table I. No change in $A(\theta)$ was detected when the sample was rotated about the c axis, with c perpendicular to H_{dc}. The g factor was found to be constant (within the experimental error) under both of the above rotations, and is also given in Table I.

When hot-pressed BN and compression-annealed pyrolytic BN are exposed to γ rays, only the carbon-associated-type three-boron centers are produced. The intensity of the EPR signal of this center was saturated at high γ-ray doses of several Mrad. After electron irradiation no noticeable increase in the EPR signal of this center could be observed, but the new three-boron center appeared. The intensity of the EPR lines of the new centers increased linearly with the irradiation time, up to 16 h of electron irradiation, with no indication of saturation. The EPR signal of the

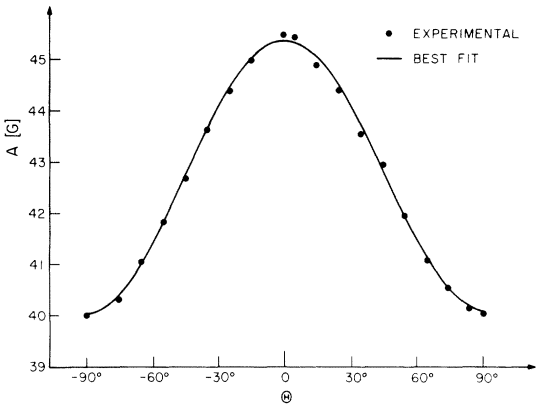

FIG. 2. Angular variation of the hyperfine splitting A between two adjacent EPR lines of an electron–irradiation–produced three-boron center. This splitting refers to the interaction of the unpaired electron with ^{11}B nuclei. The dots represent the experimental points, and the solid line the computed best-fit curve. θ represents the angle between the c axis and the external magnetic field H_{dc}.

electron-irradiation-produced centers can be bleached by heating to temperatures above 700 K. After electron irradiation, samples were annealed in air at different temperatures, for 24 h periods. We have found that following annealing at temperatures below 1200 K: the EPR spectrum can be completely regenerated by γ irradiation. For annealing at temperatures between 1200 and 1600 K, the EPR spectrum could be regenerated only partly (the intensity of the regenerated spectrum decreased with increase in the temperature of the heat treatment). Above 1600 K the regeneration of the spectrum by γ irradiation was not possible, and only after another electron irradiation did the spectrum reappear.

The method of combining isochronal and isothermal annealing[5] was used to investigate the thermal stability of the electron-irradiation-produced EPR centers. Isochronal annealing was carried out in the temperature range between 300 and 1200 K and exhibited a sharp knee at about 750 K. Isothermal annealing was carried out at 768 ± 2 K. From the results of the isochronal and isothermal annealings, an activation energy of $E = 2.0 \pm 0.3$ eV was obtained.

DISCUSSION

The conclusive evidence for the identification of the electron-irradiation-produced paramagnetic centers as three-boron centers was done by a computer simulation of the observed EPR spectrum. In generating the simulated spectrum, we followed the method used by Römelt[6] for three-boron centers. However, in our case, owing to the much

TABLE I. Resonance parameters of three-boron centers in hexagonal BN.

	$A_{\parallel}$ (G)	$A_{\perp}$ (G)	g	Reference
Carbon-associated three-boron center	6.58 ± 0.007	7.85 ± 0.007	$g_{\parallel} = 2.002\,26 \pm 0.000\,02$ $g_{\perp} = 2.003\,21 \pm 0.000\,02$	Moore and Singer, Ref. 4
Electron-irradiation-produced three-boron center [a]	45.3 ± 0.5	40.0 ± 0.5	$g = 2.0020 \pm 0.0008$	This paper

[a] Results for the electron-irradiation-produced center refer to the resonance lines due to interaction with ^{11}B nuclei.

larger hyperfine splitting, second-order effects had to be taken into account. The simulated spectrum for our case was calculated using a Gaussian line shape, with an 8-G peak-to-peak linewidth of the first derivative of the absorption line and a hyperfine splitting of 45.3 G. These values of linewidth and hyperfine splitting were taken from our experimental results for H_{dc} along the c axis. The computer-simulated spectrum, shown in the lower part (II) of Fig. 1, exhibits a very close resemblance to the experimental spectrum [Fig. 1(I)]. This strongly supports our assignment of the EPR spectrum in electron-irradiated BN to an electron interacting with three neighboring boron nuclei. It can be seen from Fig. 1 that the EPR spectrum of the electron-irradiation-produced center consists of two groups of lines: a group of ten stronger lines, mainly due to interaction with ^{11}B nuclei, and a group of nine weaker lines (each flanked by two strong lines), including also interaction with ^{10}B nuclei. These weaker lines could not be resolved in the carbon-associated three-boron centers because of the relatively small hyperfine splitting.

In Papers I and II of this work[1,2] the nature of the carbon-associated three-boron center was discussed. It was shown that this type of defect consists of an electron trapped in a nitrogen-ion vacancy, surrounded by three nearest-neighbor boron ions. The presence of carbon atoms in the vicinity of the vacancy was found to be essential[4] for the existence of this center. It was also shown that the trapped electron has a π character, and is substantially delocalized on the carbon impurity.[2]

The model proposed for the new center reported here is that of an electron trapped in a nitrogen vacancy surrounded by three neighboring boron atoms (F center). The vacancy is produced by 550-kV electrons (by displacing nitrogen ions from their lattice sites) and this process occurs even in "carbon-free" hexagonal BN. This is in contrast to the case of the carbon-associated three-boron centers, where the presence of carbon is essential, and thus these centers cannot be produced by electron irradiation in carbon-free BN.

The proposed model accounts well for the behavior of the EPR spectrum, and for the marked difference between this center and the carbon-associated one. The anisotropy of the hyperfine splitting in highly oriented compression-annealed pyrolytic BN is given in Eq. (1). From this anisotropy it can be shown[7] that the unpaired electron has a considerable π character. Moreover, the much larger hyperfine splitting in our case, as compared with the carbon-associated three-boron center (see Table I), indicates clearly that the unpaired electron is much more delocalized on the neighboring boron nuclei in the carbon-free point defects in hexagonal BN. Simple calculations[7] can be used to obtain approximate values of C_s^2 and C_p^2, the respective unpaired σ and π electron densities on the nearest-neighbor boron atoms: $c_s^2 = 0.046$ and $c_p^2 = 0.08$. Therefore approximately 24% of the electronic charge of the π orbital is delocalized on the three nearest-neighbor boron atoms. This delocalization is about four times larger than in the case of carbon-associated three-boron centers.

These results agree with the theoretical studies given in Paper II of this work,[2] which have shown that the electron is trapped in a π defect orbital, with its charge symmetrically distributed on the three neighboring boron atoms, and that the carbon impurities decrease the degree of delocalization on the boron atoms.

The thermal annealing experiments indicate that the electron trapped in the electron-irradiation-produced vacancy is located approximately 2 eV below the conduction band. This is also in fair agreement with the theoretical calculations of Paper II. The thermal treatment of the electron-irradiated hexagonal BN samples shows that heating to temperatures up to 1200 K releases the trapped electrons from the vacancies but does not destroy the vacancies themselves. Thus, after this bleaching, the EPR signal can be regenerated by ionizing radiation. An annihilation of the vacancies begins above 1200 K and is completed around 1600 K, where an electron irradiation is required to regenerate the EPR signal.

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