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Point defects in hexagonal boron nitride. I. EPR, thermoluminescence, and thermally-stimulated-current measurements

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When hexagonal boron nitride is exposed to ionizing radiation two types of paramagnetic centers
appear: three-boron centers and one-boron centers. Results of electron paramagnetic resonance,
thermoluminescence, and thermally-stimulated-current measurements associated with these centers are described, and a model is proposed to explain these results. The model is consistent with views of
others investigators on the role of carbon impurities in hexagonal boron nitride, and with the
hypothesis that the three-boron centers are F centers. The three-boron centers and one-boron centers
were found to introduce trapping levels at 1.0 and 0.7 eV, respectively, below the conduction band. It
is suggested that carbon impurities produce luminescence centers, with an energy level at about 4. 1 eV below the conduction band. Ionizing radiation frees electrons from these levels into the conduction
band. Some of the electrons may then be trapped either in three-boron

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disappear upon further heating.
Moore and Singer confirmed the existence of
the two types of three-boron centers, and proved that carbon impurities were necessary for the production of the centers. They also found a direct relation between the concentration of the three-boron centers and the strength of the yellow color, These workers also observed that both the g factor and the hyperfine splitting of the ten-line spectrum were anisotropic, and suggested that the unpaired electron had a m character.
Moore and Singer assumed the thermal produc-tion of the three-boron centers to be due

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TBC III I I I I III

FIG. l. EPR spectrum
of p-irradiated hot-pressed
boron nitride. Positions of
the one-boron-centers

(OBC) and three-boron-
centers (TBC) lines are in-
dicated.

OBC

5200
I

5400
I

5600 G

were carried out in

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(o)

U

D

~~ 0.5—
O~
CL

E
U

K
Q
4J

2500

'IAtavelength (0)

TBC
OBC

+ Tm =700'K
OTrn =380 K
a Trn = l00'K

5500

In the search for other thermally bleachable
centers we performed measurements at low tem-
peratures. The samples were y irradiated at VV 'K, and EPR measurements were carried out at the same temperature, but no new EPR centers
were found.

B. Glow-curve measurements

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Useful information can be gained by combined
EPR and glow-curve measurements. 6' ~ The for-
mer can help to establish the chemical nature of
the defect and the symmetry of the charge distribu-tion, while the latter may be used to determine the energy of the trapping level.
Our measurements were carried out on grade
HP samples which had been exposed to ionizing radiation (uv, x rays, or y rays). Some of the re-sults on the thermoluminescence and the thermally stimulated current measurements of samples ex-cited by x rays at room temperature were reported elsewhere. Two glow peaks at 380 and at 700 K
were observed, and are shown in Fig. 3(b). The
activation energies of the two peaks were deter-
mined by the "initial-rise" method, and found to
be 0. V + 0. 1 and 1.0 + 0. 1 eV for the 380 and 700 'K
peaks, respectively. Using uv light for the exci-
tation we were able to measure the excitation spec-

FIG. 2. (a) Excitation spectrum of the EPR signals as measured at 300'K. (b) Excitation spectrum of the thermoluminescence {TI.) peaks at 100, 380' and 700'K.

affected mainly by green light (5500 + 100 A) and the three-boron-center signals, by blue light (4500 +100 A). We have not succeeded in measuring the detailed spectrum of optical bleaching. Compression-annealed pyrolytic boron nitride resembles a single crystal in many respects, which is one of the reasons why Moore and Singer chose it for studies of the anisotropy of the three-boron centers. We carried out similar measurements on one-boron centers in CAPBN, and measured the anisotropy of the g factor and of the hyperfine splitting ~between the two central EPR lines. The sample was rotated about an axis in the plane of the boron nitride hexagons (perpendicular to the c axis), thus

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t50

V)
EO

O—Ioo
C

CL

CO

5 50

0

-90 %0 -30 0 30 60
Angle between H and the c-axis(deg)

90

FIG. 4. Hyperfine splitting ~between two one-boron. — center EPH lines as function of the angle 8 between c axis and the external magnetic field Hz,.

C. Photoluminescence and phosphorescence

Photoluminescence measurements were carried

out only on grade HP hot-pressed powder samples. They were excited by uv at or below room tempera-ture, and a blue photoluminescence was observed. The excitation spectrum was found to peak at 3200 A, and the emission spectrum covered the region 3900-5000 A, with a peak near 4200 A. These re-sults are similar to those reported by others, although we were not able to observe the fine struc-ture.

On excitation by uv or x rays at VV K, we ob-served a blue phosphorescence after termination of the excitation. The phosphorescence emission looked to be similar to that of the photolumines-cence. At VV 'K the phosphorescence decayed

trum of the peaks, and found that they were very
similar

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Conduction Band

Eg 4. I eV

-O.S eV

-I.O eV ST
OBC
TBC

Valence Band

FIG. 5. Schematic energy

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that the luminescence centers are associated with
carbon. The centers are assumed to introduce the

energy level C (Fig. 5) at 4. l eV below the conduc-
tion band, which fits the peak of the excitation spec-
trum. Upon heating, the trapped electrons are ex-
cited to the conduction band, and emit blue light light

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E.

)Tj ET BT /X 8.76 T5 T5Tf 316 656.67 (toancomb

s4j ET BT /BT /Xi7 8.375.0388455.19 T85(1966).

4G.