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Boron, the Dominant Acceptor in Semiconducting Diamond

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A study has been made to determine the nature of the acceptor center in laboratory-grown semiconducting diamonds. Analyses for nitrogen, aluminum, boron, and uncompensated-acceptor content of aluminum and boron-doped crystals have shown that (i) the aluminum content of inclusion-free crystals is very low, (ii) there is not enough aluminum to account for the acceptor content, (iii) the nitrogen content is very low and only a small degree of compensation by deep-lying nitrogen donors could exist for many semiconducting diamonds, and (iv) there is a good correlation between boron content and acceptor content. These results indicate that boron is the dominant acceptor in laboratory-grown semiconducting diamond, and not aluminum as has been assumed previously by a number of authors. These results, when combined with other data on resistivity and activation energy for conduction, indicate that the dominant semiconducting properties of both natural and laboratory-grown diamond are due to one acceptor, boron, at different concentrations. Previous papers on laboratory-grown semiconducting diamonds which based arguments on the large aluminum content and the assumed high nitrogen content are critically reexamined.

I. INTRODUCTION

The purpose of this study was to determine the nature of the acceptor center in semiconducting diamond. The qualitative and quantitative results presented here indicate that the dominant acceptor is boron, and not aluminum, as has been assumed previously by a number of authors.

Semiconducting, or type-II b,[1] diamonds, were first recognized by Custers.[2,3] A number of papers have been published subsequently on their electrical and optical properties. The activation energy for conduction was found to be approximately 0.35 eV[4,5] and the conduction to be p type.[5] Certain optical-absorption features in the infrared part of the diamond spectrum are present in type-IIb diamond only and it was suggested that the major absorption peak was associated with electronic transitions from a ground state to an excited state.[6] The strength of this major absorption peak correlated with the number of uncompensated-acceptor centers at room temperature.[7] These latter two papers, Refs. 6 and 7, also showed that resistivity and Hall-effect measurements led to unrealistic results for the hole effective mass if one assumed that only acceptors were present. It was thus concluded that there must be partial compensation by donors.

There is substantial experimental and some theoretical evidence that nitrogen is the principal donor in diamond and that it produces a deep donor level. Nitrogen can be present in natural diamonds in large amounts, and density and lattice-constant measurements required a substitutional site.[8] Electron-paramagnetic-resonance techniques also showed that the nitrogen was present in substitutional sites in diamond.[9] Activation analyses confirmed that nitrogen could be present in substantial amounts, but that arsenic and antimony, two other group-V elements that might also act as donors, were present only in amounts of $< 5\times10^{-4}$ atomic ppm.[10] Phosphorus, another possible donor, could not be detected using this method. However, experiments in our laboratory indicated that growing diamonds in systems containing phosphorus produced no significant changes in their electrical or optical properties. The donor level is deep lying, approximately 4 eV below the conduction band, as indicated from luminescence data on natural and laboratory-grown diamond.[11,12] More recent atomic-orbital–molecular-orbital calculations predicted that the introduction of substitutional nitrogen into the diamond lattice produced a deep donor state.[13] The depth of the nitrogen level, approximately 4 eV below the conduction band, precludes n-type conduction at room temperature.

The determination of the acceptor center has not been as straightforward. Various chemical-impurity measurements on natural diamonds have shown the presence of many elements, with aluminum present in most crystals.[14–17] Subsequent activation-analysis studies also showed aluminum was present, but that gallium and indium, two other group-III elements that might act as acceptors were present in amounts of only $<5\times10^{-4}$ atomic ppm.[10] Boron could not be detected using this method. Wentorf and Bovenkerk had reported growing small p-type semiconducting diamonds by addition of boron, aluminum, or beryllium to the growth media and suggested that some of the natural type-IIb diamonds contain boron as an acceptor impurity.[18] A number of authors have proposed that aluminum is the principal acceptor in diamond.[6,12] Dean *et al.*,[11] by comparing acceptor concentration as obtained from Hall data and alumimum concentration as determined by neutron activation analysis on three natural type-IIb diamonds, concluded that the acceptor center was due to isolated substitutional aluminum impurities. This conclusion has been assumed correct for both natural and laboratory-grown diamonds in a number of subsequent papers.[19–23] However, Wedepohl[24] showed that the then current evidence did not warrant such an unambiguous identification and concluded that other elements, in particular boron, should not be excluded as possibilities. Recently, a more precise study by Collins and Williams[25] concluded that aluminum cannot be the acceptor in semiconducting diamond. For each crystal examined, the aluminum content as obtained by neutron activation analysis was substantially lower than the acceptor content as determined by Hall data. On the basis of conversations with the present author, Collins and Williams mentioned a number of my preliminary results that were obtained on laboratory-grown semiconducting diamonds including my conclusion that boron is the dominant acceptor in diamond.

The purpose of this paper is to present more detailed qualitative and quantitative evidence that the dominant acceptor in diamond is boron, and cannot be aluminum as has previously been assumed. The significance of the present results with respect to certain previous papers will also be discussed.

II. EXPERIMENTAL

The diamonds examined in this study weighed from 25 to 140 mg and were 2–5 mm in size. Analyses were made for nitrogen, boron, aluminum, and uncompensated-acceptor content. Not all analyses were made on all the diamonds; sometimes diamonds grown under identical growth conditions were used to complete a series of analyses. The diamonds were grown by the temperature-gradient method.[26,27] These larger diamonds were necessary for certain key analyses, in particular, the neutron activation analyses for aluminum. Studies in our laboratory have indicated that the smaller, more rapidly grown General Electric diamonds such as those examined by others[11] can readily give inaccurate results for dispersed aluminum content because of the presence of inclusions which are difficult to detect and remove. This problem will be described more fully in the discussion. In some of the diamonds the distribution of blue coloration was not homogeneous; this is taken into account in the discussion.

The nitrogen content was obtained by vacuumfusion analysis at 2100 °C, as this procedure was known to give total nitrogen content for synthesized diamonds.[1] The diamonds used in these nitrogen analyses had no inclusions when examined microscopically at 100× magnification.

The boron content was determined using activation analysis and plastic particle track detectors.[28]

The aluminum content was obtained using neutron activation analyses[29] with a sensitivity of 4×10^{-9} g. The fast-neutron flux in the reactor meant that any silicon present could conceivably give a false aluminum reading in the ratio that 65-ppm silicon were equivalent to 1-ppm aluminum. This unlikely, but possible, interference does not alter the conclusions reached in this paper. Also, other data of ours indicate the silicon content of these crystals would be very low.

The uncompensated-acceptor content, $N_A - N_D$, was obtained by measuring infrared-absorption spectra and using the calibration curve of Collins and Williams,[25] or its extrapolation. In practice, the integrated absorption intensity of the 2800-cm^{-1} (0.347-eV) absorption band was not calculated for each diamond, but only the maximum absorption coefficient $\Delta\alpha$ from the same baseline as one would use for obtaining the integrated absorption.[25] The double-beam spectrometer output was actually plotted on paper that gives the absorbance A. The absorption coefficient $\Delta\alpha$ to the base e was obtained from $\Delta\alpha = 2.3\,\Delta A/t$, where t is the thickness of the crystal. Data from semiconducting diamonds of different dopant levels showed that $I/\Delta\alpha = 0.85\times10^{-2} \pm 20\%$, where I is the integrated area of the 2800-cm^{-1} band (eV cm^{-1}) and $\Delta\alpha$ is the absorption coefficient of the 2800-cm^{-1} band (cm^{-1}). Integrated areas of the crystals examined ranged from 1.5 to 144.0 eV cm^{-1}. This is equivalent to a range of $N_A - N_D$ of 0.07 to 6 atomic ppm. For certain diamonds, the acceptor absorption band at 2800 cm^{-1} was too strong for accurate measurement and a correlated band at 1290 cm^{-1} was used to determine the uncompensated-acceptor content. Data showed that

$$(\Delta\alpha \text{ at } 2800\ \text{cm}^{-1})/(\Delta\alpha \text{ at } 1290\ \text{cm}^{-1}) = 22 \pm 20\%$$

over the range

$$1.30 \leq (\Delta\alpha \text{ at } 2800\ \text{cm}^{-1}) \leq 144.0\ \text{cm}^{-1}\ .$$

Hence, reasonably accurate values of $N_A - N_D$ could be obtained by measuring the maximum absorption coefficient at 2800 or 1290 cm^{-1} and using the appropriate calibration factors described above, in conjunction with the calibration curve of Collins and Williams.[25]

This method of obtaining uncompensated-acceptor concentrations gives values that are in good agreement with those obtained from C-V (capacitance-voltage) measurements.[30] For example, infrared measurements on several diamonds gave uncompensated-acceptor concentrations of 1.8×10^{17}, 2.8×10^{17}, and 2.5×10^{18} cm^{-3}. The respective values from C-V measurements were 0.9×10^{17}, 3.4×10^{17}, and 2.4×10^{18} cm^{-3}.

Figure 1 shows a redrawn spectrum of a light-blue boron-doped laboratory-grown semiconducting diamond; the absorption bands at 2800 and 1290 cm^{-1} are marked.

III. DISCUSSION AND RESULTS

Both insulating and semiconducting diamonds have been grown and examined in our laboratory for a number of years,[1,18,26–28,31,32] with some of these crystals being examined for optical and electrical properties by other investigators.[11,12,19,20] The semiconducting crystals were of special interest and by comparison with natural diamonds, it appeared that both natural and laboratory-grown crystals had the same acceptor center.[11,19,20,23,25] Activation analyses had shown that both aluminum-doped and blue boron-doped laboratory-grown diamonds contained approximately 150-ppm aluminum which was assumed to be the acceptor, and yet optical-absorption data on the same crystals showed widely differing amounts of uncompensated acceptors.[11,23] The conclusion reached, based on the fact that most natural and laboratory-grown diamonds contain nitrogen, was that there was a wide range of compensation due to a varying amount of deep-lying nitrogen donors. The concentration of donors needed was at least 100 atomic ppm. It was then argued that the available data on laboratory-grown semiconducting diamond could be explained as follows.

(a) For the colorless aluminum-doped diamonds, the deep nitrogen donors compensated the aluminum centers, but since there was an excess of aluminum, one would have p-type conduction due to the uncompensated aluminum acceptors.

(b) Addition of boron formed an acceptor center with a smaller ionization energy than aluminum, which was then preferentially compensated by nitrogen donors. This left a large concentration of uncompensated aluminum to give conduction. This also meant that the aluminum-acceptor absorption band would be more intense, the continuum absorption would extend further into the red part of the visible spectrum, and the boron-doped diamonds would appear blue.

These hypotheses appeared to explain the electrical and optical properties of many aluminum and boron-doped diamonds grown in our laboratory, except that increasing the aluminum content never gave blue diamonds. This was puzzling. From hypothesis (a) above, one would expect blue diamonds if larger amounts of aluminum were added, since one would have larger numbers of uncompen-

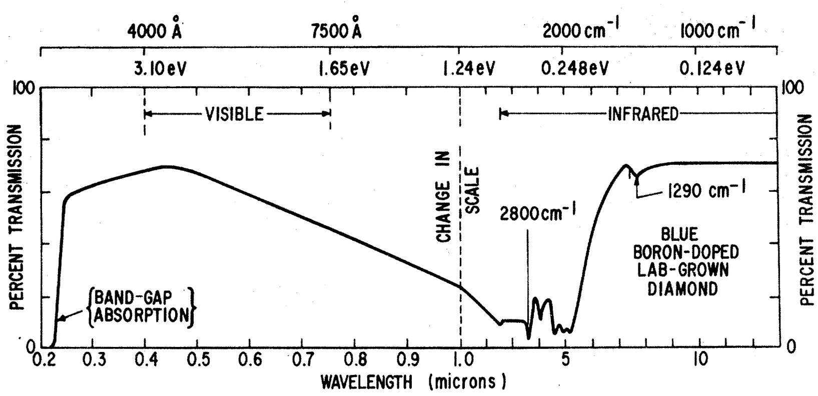

FIG. 1. Spectrum of light-blue boron-doped laboratory-grown semiconducting diamond. Absorption bands at 2800 and 1290 cm^{-1} are marked.

sated aluminum acceptors. This assumes the nitrogen content remains the same and that there was no solubility limit for aluminum in the aluminum range investigated.

These hypotheses, based on having large total aluminum-acceptor contents of approximately 150 ppm as obtained by others from neutron activation analysis for aluminum, were tested by us in several experiments.

Hypothesis (a) was ruled out by our nitrogen analyses on some large, inclusion-free, colorless, aluminum-doped crystals which showed < 2.5-atomic-ppm nitrogen. For the aluminum-doped crystals, this was approximately 60 times less nitrogen than that needed to explain the difference between the ~150-ppm aluminum found by others in the smaller semiconducting diamonds and assigned to the acceptor, and the ~1 ppm of uncompensated acceptors found by others from infrared spectra. This assumes that the dispersed aluminum and nitrogen contents of these larger, inclusion-free aluminum-doped crystals are the same as for the smaller aluminum-doped crystals.

Hypothesis (b) was ruled out by our analysis of an inclusion-free, blue boron-doped diamond which showed < 0.2-ppm nitrogen. Preliminary Hall C-V measurements also indicate that the donor content is much less than the acceptor content.[33] Again, there was insufficient nitrogen to explain the difference between the amounts of aluminum and uncompensated acceptor found by others.

Some of the discrepancies would be resolved if it were shown that only small amounts of dispersed aluminum were present in truly inclusion-free laboratory-grown semiconducting diamond. This would infer that most of the high aluminum content of ~150 ppm found in smaller General Electric diamonds was due to the presence of metallic inclusions and that the amount of aluminum that could be assigned to the acceptor was small. The presence of a small aluminum content and virtually no nitrogen would then mean that one could have, not the same high aluminum concentration with varying amounts of compensation, but actually a range of lower aluminum-acceptor concentrations with little or no compensation. Under these conditions, hypothesis (a) would still be valid; aluminum could still be the acceptor. However, hypothesis (b) would still be untenable. If, indeed, little or no nitrogen is present but aluminum and boron are, then one would expect to see some indication of a shallower level due to the boron. However, except for the degree of intensity of the acceptor absorption bands, no differences have been seen in the absorption spectra of approximately 50 semiconducting diamonds doped with widely different levels of aluminum and boron.

The analyses for aluminum and boron in laboratory-grown semiconducting diamond are presented in Table I. These data completely rule out the aluminum-acceptor hypotheses (a) and (b) and lead to the conclusion that the dominant acceptor center in diamond is boron. Data are given on one colorless and four blue semiconducting laboratory-grown diamonds. In columns one and two are listed the individual diamonds and dopants used. In the third column is the integrated area or effective integrated area of the 2800-cm^{-1} acceptor absorption band obtained as described above. The fourth column lists the number of uncompensated acceptors $N_A - N_D$ predicted by combining the data of column three and the calibration curve of Collins and Williams.[25] Column five lists the aluminum contents in atomic ppm as determined by neutron activation analyses. Column six lists the boron content determined by activation analysis and plastic particle track detectors.

The data will now be examined more critically.

In column four the desired value is N_A, not the $N_A - N_D$ value obtained from infrared spectra, since it is N_A that is compared with aluminum and boron content. However, the nitrogen analyses show the nitrogen content is < 2.5 and more probably < 0.2 atomic ppm, since all the crystals were grown under similar conditions, except for the boron-dopant material. Hence, the N_A value is

TABLE I. Comparison of aluminum, boron, and uncompensated-acceptor contents for laboratory-grown semiconducting diamonds.

No.	Diamond and dopant Description	Integrated area at 2800 cm^{-1} (eV cm^{-1})	Predicted $(N_A - N_D)$ (atomic ppm)	Aluminum content (atomic ppm)	Boron content (atomic ppm)
52	Colorless Al	0.94×10^{-2}	0.042 ± 0.02	0.022 ± 0.008	<0.5
48	Blue Al + B	6.5	0.37 ± 0.18	0.043 ± 0.010	<0.5
43	Blue Al + B	78	3.8 ± 1.9	...[a]	4 ± 1
60	Blue Al + B	87	4.6 ± 2.3	...[a]	15 ± 5
1433	Blue Al + B	≥ 54	$\geq 2.3\pm1.1$	0.22 ± 0.06[b]	...[a]

[a] Not measured.

[b] Had inclusions. Aluminum content is 0.05 atomic ppm when allowance is made for inclusions. See text.

approximately equal to the $N_A - N_D$ value that is obtained from infrared spectra. For the first two samples, Nos. 52 and 48, if one assumes $N_D = 0$, there is not enough aluminum to account for the acceptor content. If $N_D \neq 0$ then the discrepancy between N_A and the aluminum content is even larger. The aluminum contents of crystals No. 43 and 60 were not obtained because of several inclusions. The aluminum content for crystal No. 1433 is discussed later.

The boron contents reported for crystals No. 52 and 48 represent the limit of sensitivity, but the values of < 0.5-atomic-ppm boron are not inconsistent with the $N_A - N_D$ concentrations. The boron values would be inconsistent if $N_D > 0.5$-ppm nitrogen for No. 52 or $N_D > 0.2$-ppm nitrogen for No. 48, but our data indicate this is not the case. The boron concentration of sample No. 43 agrees well with the number of uncompensated acceptors. For sample No 60, the boron concentration is appreciably higher than the number of uncompensated acceptors. This apparent discrepancy is probably due to the nature of the diamond and the technique used to measure the boron. It was known that this blue diamond, No. 60, was deeper blue in the region in which the boron was determined. Therefore, if boron is causing the blue color, as seems probable from the other data, then the measured boron concentration would be larger than the $N_A - N_D$ value. The technique used for measuring boron content samples a surface layer a few microns thick.[28] On the other hand, the $N_A - N_D$ value obtained from infrared absorption measurements is an average of regions of both low and high uncompensated-acceptor content. Hence, for No. 60, the boron analysis would be expected to give a somewhat higher boron content than the $N_A - N_D$ value obtained from infrared measurements.

It is interesting to compare the aluminum contents for laboratory-grown semiconducting diamonds shown in Table I (Al < 0.22 ppm) with those reported by others (Al ~ 150 ppm).[11] It is proposed that the previous small (< 1 mm) General Electric diamonds examined by others contained small inclusions of metal. Such inclusions are very difficult to detect in small crystals, especially those with a high index of refraction. For example, one blue boron-doped "inclusion-free" crystal of 3-mm size that was examined for aluminum in this study had an aluminum content of 0.22 ppm. This crystal, No. 1433, is listed last in Table I. Although this aluminum concentration was a factor of 10 less than the number of uncompensated acceptors, and also rules out aluminum as the acceptor, it was 5–10 times the aluminum concentration of the other laboratory-grown semiconducting diamonds studied. More careful microscopic examination later showed several small rodlike inclusions of the order of 10-μm diameter by 150-μm length. If these inclusions were filled with the metal used in the growth cell and the amount of aluminum in the inclusions were calculated and subtracted from that found by neutron activation analysis, then the aluminum concentration would be 0.05 ppm, approximately the same as for the other crystals examined. It would be difficult to observe and correct for such inclusions in smaller-sized crystals.

Several blue, natural, type-IIb crystals were also examined for comparison purposes for color, conductivity, and optical-absorption properties. They could not be distinguished from blue, lightly boron-doped laboratory-grown diamonds. Even the half-widths of the uncompensated-acceptor absorption band at 2800 cm^{-1} were identical. The data indicate that the same acceptor center, boron, is responsible for the semiconducting properties of both laboratory-grown and natural diamonds. In retrospect, the fact that the acceptor is boron and not aluminum is not inconsistent with the smaller covalent radius of boron (0.82 Å) compared with aluminum (1.18 Å).

The large possible errors for the $N_A - N_D$ values reflect, not only the errors due to converting infrared absorption measurements to $N_A - N_D$ values, but also the nonhomogeneity of certain crystals. In this respect, blue, semiconducting, type-IIb laboratory-grown and natural diamonds are also similar.[5,7] Despite this nonhomogeneity, the basic conclusions remain valid.

Other chemical impurities in substitutional or interstitial sites might also be considered candidates for the acceptor. Our chemical analyses were not all-inclusive so other elements cannot be definitely ruled out on a quantitative basis, as has aluminum. However, our qualitative results, based on growing many large diamonds under controlled conditions, do appear to rule out other elements. Presence of aluminum or titanium in the growth chamber gives, at times, colorless semiconducting diamonds that show the uncompensated-acceptor absorption band at 2800 cm^{-1}. However, increased amounts of aluminum or titanium in the growth chamber do not produce blue diamonds since the 2800-cm^{-1} absorption band does not become strong enough. Beryllium doping has been reported to produce semiconducting diamonds.[18] Our experiments indicate this is true, but massive additions of beryllium do not produce blue diamonds. We believe that the presence of conductivity and the uncompensated-acceptor absorption band at 2800 cm^{-1} in diamonds grown in systems not deliberately doped with boron is due to (i) the absence of nitrogen as a compensating donor in the diamonds and (ii) the presence in the growth chamber of small amounts of boron contaminant that enters the diamonds and produces conductivity. Only by the systematic addition of boron can diamonds be produced that go from colorless, to light blue, to deep blue, to black. The boron can be in the form of elemental boron, B_4C crystals, or small boron-doped diamonds. It appears highly unlikely that an impurity element would be present in the same relative amounts in all three forms of boron dopant. Also, the total acceptor content in the diamond agrees well with the total amount of boron dopant used.

In summary, the qualitative results and quantitative data presented here indicate that not enough aluminum is present in laboratory-grown semiconducting diamonds to account for their acceptor concentrations. The data also indicate that boron is the dominant acceptor in diamond, not aluminum as has previously been assumed.

IV. ANALYSIS OF PREVIOUS PAPERS

The significance of the data and conclusions presented here will be discussed with respect to certain previous studies on semiconducting diamonds. These studies include those on aluminum and acceptor content, electrical resistivity, luminescence, and optical absorption.

Studies in which aluminum was assigned as the acceptor in semiconducting diamond have been mentioned in the Introduction.[11,19-23] The data presented here indicate that (i) the aluminum content of truly inclusion-free aluminum and blue boron-doped laboratory-grown semiconducting diamond is very low, (ii) there is not enough aluminum to account for the acceptor content, (iii) the nitrogen content is low and only a small degree of compensation by deep nitrogen donors could exist for many semiconducting diamonds, and (iv) boron is the dominant acceptor center.

The role of donor-acceptor compensation in certain electrical measurements must be reexamined. For instance, electrical resistivity data indicated that the acceptor activation energy for conduction for certain laboratory-grown semiconducting diamonds was slightly less than that obtained for natural semiconducting diamonds in the temperature range where the "normal" acceptor ionization energy E_A ($1/\rho \propto e^{-E_A/kT}$) determines the slope of the ρ-vs-$1/T$ curve.[20] This lower E_A was then attributed to the high concentration of compensated acceptors. However, this view is in doubt since there appears to be little nitrogen to provide compensation in laboratory-grown semiconducting diamonds. This slight decrease in activation energy seems more probably due to the increased acceptor concentration.

Williams *et al.*,[23] in examining electrical characteristics of several semiconducting diamonds, listed compensation ratios that ranged up to 99.7%. These ratios were determined by assuming N_A equaled the aluminum content and deducing donor concentrations in the $(1-2)\times 10^{19}$-cm^{-3} range. However, for inclusion-free semiconducting crystals examined by us, no definite evidence of nitrogen has ever been detected; upper limits were in the $< 0.36\times 10^{17}$- to $< 4.6\times 10^{17}$-cm^{-3} range. One crystal was listed by Williams *et al.* with $N_A - N_D = 3 \times 10^{17}$ cm^{-3} and a compensation ratio of 98.5%. A crystal examined in the present study had nearly the same value for $N_A - N_D$ ($= 2.9\times 10^{17}$ cm^{-3}), and a measured nitrogen content of $< 0.36\times 10^{17}$ cm^{-3}. The compensation ratio for this latter crystal is < 15%. If, indeed, nitrogen is the donor and the nitrogen contents are roughly the same for previously examined crystals and those examined by us, then previously published compensation ratios appear much too high. Williams *et al.* also noted that a higher E_A value of 0.37 eV for one laboratory diamond compared to the E_A value of 0.35 eV for another was consistent with the increase in compensation ratio, which went from 98.5 to 99.7%. In view of the large possible errors in compensation ratios, it is more reasonable that the higher E_A value is due to a lower acceptor concentration.

The luminescence of laboratory-grown semiconducting diamonds has been partially attributed to recombination radiation at donor-acceptor pairs, where nitrogen was assigned as the donor and aluminum as the acceptor.[11,12] Several comments can be made in light of the results presented here. The arguments to justify the lack of a photoexcitation spectrum due to boron[11] are immaterial, since the spectra assigned to aluminum are really due to boron. The relative weakness of emission from an aluminum-doped synthetic crystal with respect to the amount of compensated aluminum[11] can be partially resolved. There need not be a correlation with the aluminum content since the acceptor is boron. Discrepancies still appear with respect to emission assigned to diffuse donor-acceptor pairs. The emission data suggest that the concentration of compensated-acceptor centers in an aluminum-doped laboratory-grown crystal may be $10^4\times$ larger than for a typical natural IIb crystal.[11] However, the results presented here for aluminum-doped diamonds indicate that the nitrogen content is low, and if the compensating donor is nitrogen, then the number of compensated-acceptor centers would also be low. It would be desirable to obtain quantitative emission intensities on the larger laboratory-grown crystals to resolve this discrepancy.

Optical absorption spectra have shown a number of absorption bands in the infrared, due to the uncompensated acceptor.[6] The bands actually are due to the boron acceptor, not the aluminum acceptor as previously believed. The reported concentration broadening of the acceptor absorption band[19] should now be related to the boron contents. For crystals examined in the present study, the width (full width at half-maximum intensity) of the strongest uncompensated acceptor band at 2800 cm^{-1} (0.347 eV) ranged from 45 to 73 cm^{-1} for crystals whose uncompensated-acceptor content ranged from ~0.07 to 6 ppm (1.3×10^{16} to 108×10^{16} cm^{-3}). In view of the low nitrogen content these uncompensated-acceptor contents are nearly equivalent to total boron-acceptor contents. The bandwidth of 45 cm^{-1} for the laboratory grown semiconducting diamond is approximately the same as that for a natural semiconducting diamond of the same uncompensated acceptor concentration. It should be pointed out that measured half-widths can be in error for highly doped samples. Once the absorption is strong enough such that only $\lesssim 1\%$ of the light is transmitted, then instrumental parameters make a knowledge of the true intensity difficult and the observed half-width appears greater than it actually is. For a crystal 0.02 cm thick and using the data of Collins and Williams,[25] such a situation can occur for an uncompensated-acceptor content of $\sim 1.6\times10^{18}$ cm^{-3} or 9 ppm. It appears that some of broadening reported by Collins *et al.*[19] is due to the bottoming-out of the acceptor absorption band.

V. SUMMARY AND CONCLUSIONS

A study has been made to determine the nature of the acceptor center in laboratory-grown semiconducting diamonds. Analyses for nitrogen, aluminum, boron, and uncompensated-acceptor content of aluminum and blue boron-doped crystals have shown that (i) the aluminum content of inclusion-free crystals is very low, (ii) there is not enough aluminum to account for the acceptor content, (iii) the nitrogen content is very low and only a small degree of compensation by deep-lying nitrogen donors could exist for many semiconducting diamonds, and (iv) there is a good correlation between boron content and acceptor content. These results show that boron, not aluminum, is the dominant acceptor in laboratory-grown semiconducting diamond. When combined with other data on resistivity and activation energy for conduction, our data indicate that the dominant semiconducting properties of both natural and laboratory-grown diamond are due to one acceptor, boron, at different concentrations.

Previous conclusions on laboratory-grown semiconducting diamonds which based arguments on the large over-all aluminum content and the assumed high nitrogen content in the lattice must now be critically reexamined. The high aluminum content was no doubt due to inclusions and very little aluminum is actually dispersed in the diamond lattice. With boron as the acceptor and a low aluminum content, there is, in general, no need to assume large amounts of nitrogen and a high degree of compensation to explain the observed data. Most previous data can be explained by the fact that laboratory-grown semiconducting diamonds contain not the same acceptor content with a wide range of compensation, but different amounts of acceptors and low compensation. In some conductivity measurements, the lower values reported for the acceptor ionization energy in some samples appear due to higher acceptor content and not a lower compensation ratio. The low-temperature conductivity assigned to impurity conductivity requires some compensation, but any compensation must be small. The only serious discrepancy appears in some cathodoluminescence data which was interpreted as indicating the presence of large amounts of donor-acceptor pairs.

Any attempts to correlate optical or electrical data with acceptor content of either natural or laboratory-grown semiconducting diamond should be made with respect to boron and not aluminum content. The primary role of aluminum in the growth of laboratory-grown crystals appears to be as a getter for nitrogen.[27] Investigators of natural and, even more so, laboratory-grown diamonds should be aware of the possible presence of both macroscopic impurities and microscopic impurity segregation.

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