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Excitonic recombination radiation in undoped and boron-doped chemical-vapor-deposited diamonds

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The correlation between free-exciton and bound-exciton recombination has been investigated by cathodoluminescence in high-quality and impurity-controlled chemical-vapor-deposited (CVD) diamond films. The films are formed by [CO(5%)]/[H_2] using microwave-plasma CVD and are doped with B_2H_6 during deposition. In moderately doped (below 3×10^{18} cm^{-3}) semiconducting diamonds, the intensity ratio between bound-exciton and free-exciton recombination reflects the boron concentration in the films. It indicates the possibility for a measure of the acceptor concentration in semiconducting diamond. The temperature dependence of the recombination of the excitons bound to neutral acceptors from 80 to 160 K shows the activation energy of 50–60 meV which is comparable to the binding energy of the excitons bound to acceptors. In the same temperature range, the intensity of free-exciton recombination is almost constant due to the high exciton binding energy of 80 meV. As the boron concentration increases, the effective dissociation of the bound excitons becomes low and the emission is stable above 200 K. In heavily doped samples (above 10^{19} cm^{-3}), the direct recombination without phonon emission from the conduction band to the acceptor level takes place.

INTRODUCTION

A higher-energy optical emission from semiconductors is desired because shorter wavelength light (shorter than blue) emitting diodes or laser diodes have a lot of potentialities in solid-state physics as well as in optoelectronics. In general, a dominant edge emission higher than 5 eV (lower than 258 nm) is difficult to be realized in semiconductors. Diamond is a wide-band-gap semiconductor having a band gap of 5.5 eV at room temperature and is a suitable candidate for high-energy emission. The band structure is very similar to that of silicon (Si) in the sense that the optical transition dominantly occurs through the indirect transitions between the Δ line near the X point of the lower conduction band and the Γ point of the upper valence band. In natural semiconducting diamonds, the same types of recombination radiation of free-excitons and bound excitons as those of Si have been observed by cathodoluminescence.[1,2]

As well as high-energy optical emission, the binding energy of excitons in diamond is reported to be one of the highest in semiconductors, 80 meV in free excitons and 140 meV in bound excitons due to boron as an acceptor.[1] This means that the edge emissions are mainly due to excitonic recombination and remain in higher temperatures. In general, high-temperature excitonic emission is one of the main purposes for fabricating quantum wells in compound semiconductors for laser oscillation in lower-threshold current density. In the case of diamonds, however, if they are perfectly synthesized, the high-temperature excitons are formed in thick films or bulk without forming very thin quantum well structure.

However, there are only a few reports on exciton recombination radiation from bulk diamonds[1,2] because usually natural or high-pressure synthetic diamonds are not pure enough for excitonic recombination. Nitrogen as an impurity prevents emissions from diamonds. Compared with natural or high-pressure synthetic diamonds, there is a higher possibility of dominant edge emissions from chemical-vapor-deposited (CVD) diamonds, because the purity and dopant controllability of films are attained by clean microwave-plasma CVD diamond.[3] In CVD diamonds, the study of free-exciton[4–7] and bound-exciton[5–7] recombination radiation has been also limited, because the crystallinity of CVD diamonds is not high enough until recently.

In this study, we have observed dominant excitonic recombination radiation in high-quality CVD diamonds and investigated the relationship between bound- and free-exciton recombination as a function of boron con-

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centration in the boron-doped films at various temperatures in order to understand the correlation of excitons and acceptor centers in diamonds.

EXPERIMENT

Diamond films were formed by microwave-plasma CVD diamond using [CO(5%)]/[H_2] (Ref. 8) on Si. Only one homoepitaxial film was deposited using [CH_4(6%)]/[H_2] by the same CVD process on high-pressure synthetic diamond (100).[9] The substrate temperatures were between 850–900 °C. Boron was doped into diamonds during the depositions using B_2H_6 diluted with H_2. The boron-carbon ([B]/[C]) concentration ratios during the depositions were 50–10^4 ppm. The obtained films, except for the homoepitaxial film, are polycrystalline with a grain size of 2–3 μm having the same morphology irrespective of boron doping at the present level. The electrical conductivities of the films were measured by a four-point probe measurement. The boron concentration has been measured by secondary-ion-mass spectroscopy (SIMS). Cathodoluminescence (CL) has been observed using a scanning electron microscope equipped with a liquid-nitrogen cooling stage, a parabolic mirror, a monochromator fitted with 600 grooves mm^{-1} grating blazed at 300 nm, and a photomultiplier suitable for the 2.0–6.0-eV photon-energy region. The accelerating voltage is 20 kV and the probe current is kept at 5×10^{-7} A. The electron scanning areas were 55×45 μm. The emitted photons are collected by the parabolic mirror. Temperatures during the observations were varied from 80 to 200 K.

RESULTS AND DISCUSSION

As a function of the [B]/[C] ratio during the depositions by [CO(5%)]/[H_2] doped with B_2H_6, the concentration of boron in the polycrystalline films is shown in Fig. 1. The concentration correlates linearly with the [B]/[C] ratio of 50–10^4 ppm, but is totally low by a factor of 10–100 compared with those obtained in the films formed by [CH_4]/[H_2] doped with B_2H_6 in the same [B]/[C] ratio range[10] during deposition. Since the presence of oxygen atoms dissociated from CO or oxygen molecules is unavoidable in the reaction area, boron might be oxidized in the vapor or at the diamond surface to form boron oxides which cannot be incorporated in the diamond films. Despite the large loss of boron in the oxidation process, the boron atoms which are not affected by oxidation are incorporated in the films proportionally to the [B]/[C] ratio.

The overall CL spectrum from 6.0 to 1.5 eV of a single-crystalline undoped CVD diamond particle formed with [CO(5%)]/[H_2] several μm in size is shown in Fig. 2. It is composed of sharp edge emissions at 5.27 eV mainly due to free-exciton recombination radiation associated with phonon emissions and a broadband around 2.8 eV called band A emission. In natural type-IIb (semiconducting) single-crystal diamonds, the former represents crystal perfection[1] and the latter is observed to be located in dislocations.[11] The peak height of the edge emission in Fig. 2 is comparable to that of band A. It shows that exciton recombination is one of the major recombination processes in CVD diamonds shown in this paper. In the case of microwave-plasma CVD, the edge emissions are much more intensively observed in the films formed with CO/H_2 than with CH_4/H_2. The former is reported to be one of the best reaction gases for high-quality diamond formation.[8]

The CL spectra of polycrystalline CVD diamond with a boron concentration of 3×10^{17} cm^{-3} and a conductivity of 2×10^{-2} S/cm, and natural type-IIb diamond with about 10^{-3} S/cm in conductivity have been shown in Figs. 3(a) and 3(b), respectively. According to the notation of peaks identified by Dean, Lightowlers, and Wight,[1] peaks A_1 and B_1 are due to free-exciton recombination radiation associated with one momentum-conserving phonon, TA and TO phonons, respectively. B_2 and B_3 are associated with one and two optical phonons at $\Gamma=0$ (zone-center phonons) in addition to one TO phonon. Bound-exciton recombination radiation due

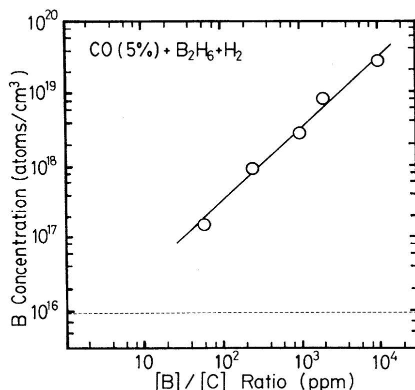

FIG. 1. Boron concentration in the polycrystalline CVD diamond formed with [CO(5%)]/[H_2] and doped with B_2H_6 as a function of the [B]/[C] ratio during the depositions. The concentration was measured by SIMS. The dashed line is the detection limit.

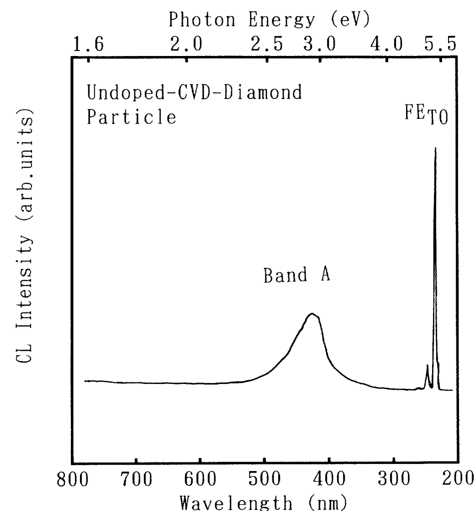

FIG. 2. CL spectrum of an undoped CVD diamond particle of 5 μm observed at 80 K. The resolution is 0.44 nm.

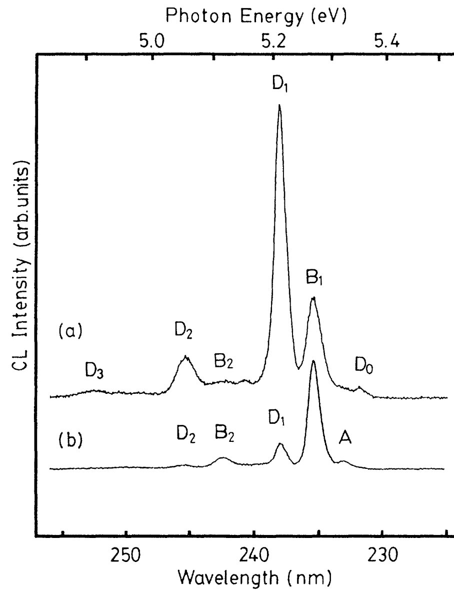

FIG. 3. CL spectra of edge recombination radiation in diamonds at 80 K. The resolution is 0.44 nm. (a) Boron-doped polycrystalline CVD diamond with a boron concentration of 3×10^{17} cm^{-3}. (b) Natural type-IIb diamond.

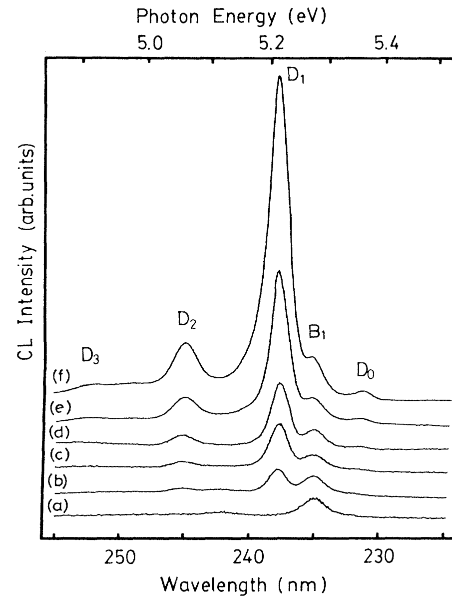

FIG. 4. CL spectra of edge emissions from boron-doped CVD polycrystalline diamond films observed at 80 K. The films were formed with [CO(5%)]/[H_2] and are 4 μm in thickness. The undoped spectrum is (a). The boron concentrations are (b) 1.5×10^{17} cm^{-3}, (c) 3×10^{17} cm^{-3}, (d) 7.5×10^{17} cm^{-3}, (e) 1.5×10^{18} cm^{-3}, and (f) 3×10^{18} cm^{-3}. The resolution is 0.9 nm.

to acceptors is observed in the peaks D_0, D_1, D_2, and D_3. The D_1 peak is associated with one TO phonon and the peaks labeled D_2 and D_3 are associated with one and two optical phonons at $\Gamma=0$ in addition to one TO phonon. The D_0 peak, clearly seen only in Fig. 3(a), denotes nonphonon radiation due to the localization of acceptors. The peak energies of B_1 and D_1 are 5.27 and 5.21 eV, respectively, and the energy difference of 0.06 eV is the binding energy of the free excitons to the acceptors. Since the peaks labeled B_1 and D_1 represent the characteristics of intrinsic and extrinsic components, i.e., the features of free excitons (FE) and bound excitons (BE), we designate B_1 and D_1 as FE_{TO} and BE_{TO}, and the intensities of them as I_{FE} and I_{BE}, respectively, later in this paper.

The CL spectra of polycrystalline diamond films doped with a B concentration of $1.5\times10^{17}-3\times10^{18}$ cm^{-3} are shown in Fig. 4. Although the total intensity slightly varies within the samples of 5×5 mm^2 in area, the intensity ratio between FE_{TO} and BE_{TO} (I_{BE}/I_{FE}) is constant inside each sample and the average intensity of FE_{TO} is almost the same in the different doping levels. Based on these facts, it is clear that the peak BE_{TO} increases as the concentration of boron increases. The half-width of the peak BE_{TO} does not vary until 1.5×10^{18} cm^{-3} and slightly increases at 3×10^{18} cm^{-3}. The recombination radiation of bound excitons and free excitons is the major recombination process in the near band edge of the CVD diamonds with boron concentration below 3×10^{18} cm^{-3}.

Figure 5 shows the intensity ratio I_{BE}/I_{FE} as a function of the boron concentration of $3\times10^{17}-3\times10^{19}$ cm^{-3} and the electrical conductivity of the films at room temperature. I_{BE}/I_{FE} increases almost linearly until 6×10^{18} cm.$^{-3}$ Above 6×10^{18} cm^{-3} the increase is not distinct and almost saturates. The natural type-IIb diamond in Fig. 3(b) having a conductivity of about 10^{-3} S/cm shows the I_{BE}/I_{FE} of 0.23 which is on the extrapolated line of Fig. 5. The intensity ratio I_{BE}/I_{FE} can be used as a measure of acceptor concentration in diamonds if no other competing recombination process emerges. The same kind of linear relationship between I_{BE}/I_{FE} and the impurity concentration has been reported in boron- or phosphorus-doped Si (Ref. 12) with an acceptor or donor concentration of $10^{11}-10^{15}$ cm^{-3}.

The saturation of I_{BE}/I_{FE} above 6×10^{18} cm^{-3} implies

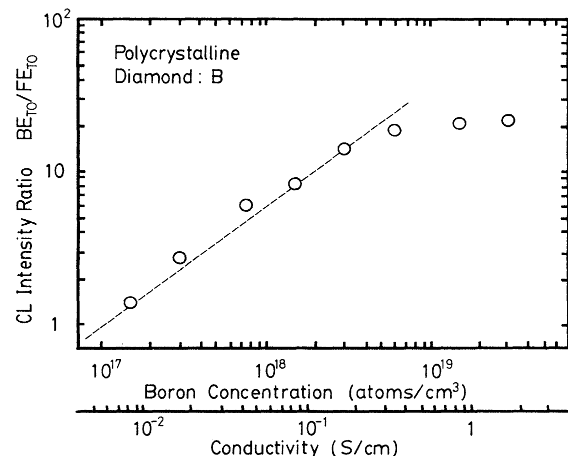

FIG. 5. Emission intensity ratio I_{BE}/I_{FE} at 80 K in boron-doped polycrystalline diamond films as a function of boron concentration and conductivity.

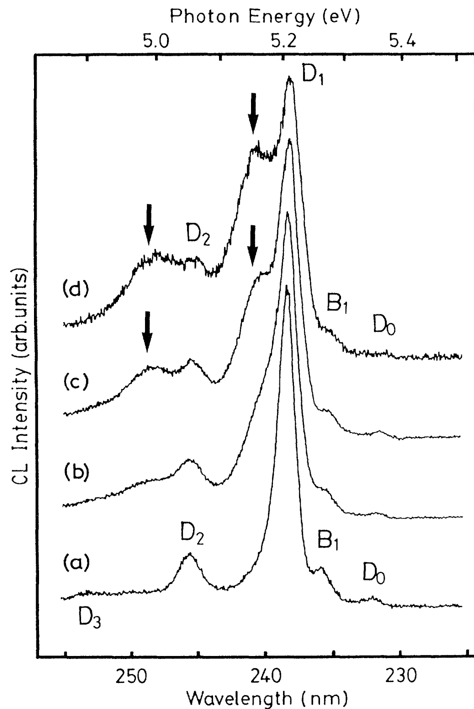

FIG. 6. CL spectra of edge emissions from boron-doped CVD polycrystalline diamond films observed at 80 K. The films were formed with [CO(5%)]/[H_2] and are 4 μm in thickness. The boron concentrations are (a) 3×10^{18} cm^{-3}, (b) 6×10^{18} cm^{-3}, (c) 1.5×10^{19} cm^{-3}, (d) 3×10^{19} cm^{-3}. The resolution is 0.44 nm. The marked peaks are 5.15 and 4.99 eV, respectively.

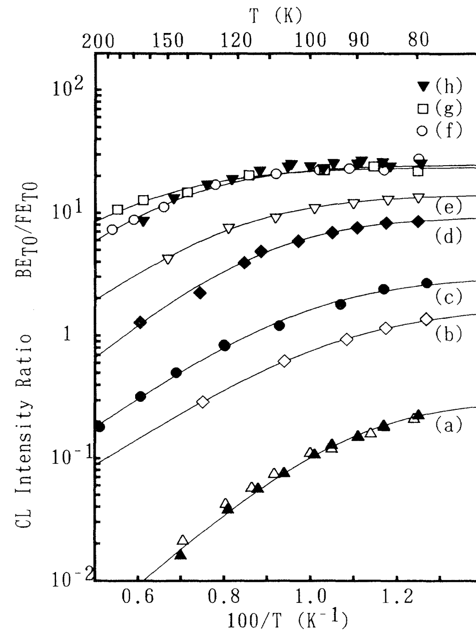

FIG. 7. Emission intensity ratio I_{BE}/I_{FE} as a function of temperature. (a) Natural type-IIb diamonds are shown in Fig. 2(a) and indicate that the measurements have been carried out when the temperature is increasing and decreasing, respectively. (b)–(g) Polycrystalline diamond films formed by [CO(5%)]/[H_2] with different boron concentration. (b) Boron concentration 1.5×10^{17} cm^{-3}. (c) 3×10^{17} cm^{-3}. (d) 1.5×10^{18} cm^{-3}. (e) 3×10^{18} cm^{-3}. (f) 1.5×10^{19} cm^{-3}. (g) 3×10^{19} cm^{-3}. (h) Homoepitaxial diamond film on (100) diamond substrate. The concentration of boron is 4×10^{19} cm^{-3}.

that there is a change in the recombination of excitons bound to acceptors. The CL spectra of the boron-doped CVD diamonds with a boron concentration of 3×10^{18}–3×10^{19} cm^{-3} are shown in Fig. 6. As the dopant increases, a shoulder emerges at the low-energy side of the BE_{TO}. In 3×10^{19} cm^{-3}, apparent peaks at 5.15 and 4.99 eV are observed. The higher-energy peak has been explained simply by the capture of electrons at the acceptor center without phonon emission or absorption. The resultant emission energy is described as $h\nu=E_g-E_A$ and 5.14 eV for the acceptor level of 0.36 eV. The lower-energy peak is a phonon-assisted transition. The energy difference of the two peaks is 0.16 eV, which is likely to be consistent with the optical-phonon energy (0.16 eV) at $k=0$ rather than the momentum-conserving TO phonon energy (0.14 eV). The resultant emission energy is described as $h\nu=E_g-E_A-E_{OP}$, where E_{OP} is an optical-phonon energy. These results indicate that the observed transition process is mainly a direct one accompanied by a phonon replica. In the case of indirect-band-gap materials, the probability of the direct process is negligible when the acceptor level is very shallow, such as boron in silicon, but becomes dominant in deep acceptors, such as indium in silicon. The latter case can be applicable for boron in diamond.[1]

The features of excitons bound to acceptors are investigated through the temperature dependence of I_{BE}/I_{FE} at different doping levels shown in Fig. 7. The intensity of FE_{TO} is almost constant in the boron-doped CVD samples with boron concentrations of 1.5×10^{17}–4×10^{19} cm^{-3} and is also unchanged from 77 to 170 K as shown in Fig. 8. Thus, the changes of I_{BE}/I_{FE} simply reflect the changes of I_{BE} at the temperature range. In Fig. 7, the intensity ratio increases as the temperature decreases and saturates at different temperatures. As the boron concentration increases, the saturation temperature decreases and the absolute intensities increase. Based on these

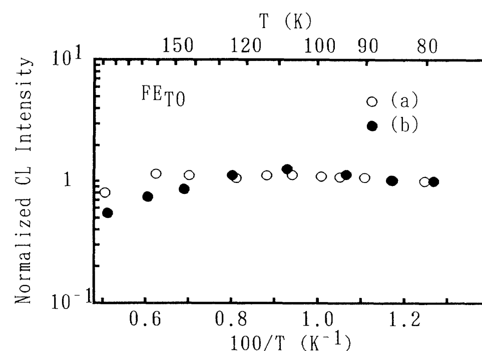

FIG. 8. Emission intensity of FE_{TO} as a function of temperature. (a) Boron-doped CVD diamond with a boron concentration of 3×10^{17} cm^{-3}. (b) Natural type-IIb diamond. The intensities are normalized at 80 K.

trends, the temperature dependence of the intensity of BE_{TO} can be described[13] by

$$I_{BE}(T)=I_{BE}(0)/[1+C\exp(-E/kT)] , \quad (1)$$

where E is the binding energy of the bound exciton, i.e., free-exciton bound-to-neutral acceptor, $I_{BE}(0)$ is the intensity of the bound exciton as T approaches 0 K, and C is a temperature-independent constant related to the Fermi level. The intensity of FE_{TO} also obeys the same kind of temperature dependence. However, below 170 K it is already almost constant (Fig. 8), i.e., saturated because of the large binding energy of 80 meV and low C. In the temperature range of 77 to 170 K, where most of the observation points in Fig. 7 are included, they can also be described by

$$I_{BE}(T)/I_{FE}(T)=I_{BE}(0)/I_{FE}(0)[1+C\exp(-E/kT)] . \quad (2)$$

In the case of the natural type-IIb diamond [Fig. 7(a)], the slope from 110 to 150 K is recognized as the activation energy of 55 meV. It almost corresponds to the dissociation energy of the free exciton from the bound exciton, i.e., the emission energy difference of 0.06 eV observed in BE_{TO} and FE_{TO} (Fig. 3). The solid lines in Fig. 7 are the fittest curves of Eq. (2) of boron-doped CVD diamonds with parameters of E, C, and $I_{BE}(0)/I_{FE}(0)$. The obtained values of C vary from 2000 to 35 and $I_{BE}(0)/I_{FE}(0)$ from 0.3 to 25 as the concentration of boron increases while E remains in the range of 50–60 meV. In the natural type-IIb diamond, $C=2000$, $E=59$ meV, and $I_{BE}(0)/I_{FE}(0)=0.3$ are obtained. In the moderately doped samples [Figs. 7(b)–7(e)], $C=140$–300, $E=50$–58 meV, and $I_{BE}(0)/I_{FE}(0)$ increases from 1.7 to 14 according to the boron concentration. In the heavily doped samples [Figs. 7(f) and 7(g)], where the boron concentration exceeds 1×10^{19} cm^{-3}, $C=35$–80, $E=52$–55 meV, and $I_{BE}(0)/I_{FE}(0)=24$–25. Figures 7(g) and 7(h) indicate that the polycrystalline and epitaxial films have the same tendency in the same boron concentration. The decrease of C in accordance with an increase of boron concentration implies that the high concentration of acceptors prevent bound excitons from being free since free excitons are easily attracted again by other acceptors before they recombine.

In the majority of samples shown in Fig. 7, the intensity ratios I_{BE}/I_{FE} are saturated at 80 K and are almost equal to $I_{BE}(0)/I_{FE}(0)$. $I_{BE}(0)$ reflects the maximum emission intensity due to bound-exciton concentration, because as the temperature approaches 0 K the probability of dissociation of the bound exciton becomes zero, in principle. It gives justification that the I_{BE}/I_{FE} at liquid-nitrogen temperature has the possibility to be used as a measure for the acceptor concentration. We have also found that, in the films with higher boron concentration, the higher emission intensity is obtained and is maintained at higher temperatures, because of the increase of $I_{BE}(0)$ and the decrease of C in Eq. (2). This fact is very advantageous for the use of BE_{TO}, such as ultraviolet photon-emitting applications.

SUMMARY

The recombination of the free exciton and the bound exciton is one of the major recombination processes at liquid-nitrogen temperature in the boron-doped CVD diamonds formed with CO/H_2 using microwave-plasma CVD. The intensity ratio of BE_{TO} and FE_{TO} reflects the boron concentration up to 6×10^{18} cm^{-3}. Above the concentration, the intensity ratio saturates because competing processes such as recombination from the conduction band to the acceptor level take place. Temperature dependence of I_{BE}/I_{FE} decreases as the concentration of boron in the films increases. It indicates that the effective dissociation of bound excitons becomes low as the acceptor concentration increases.

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