Spatially and spectrally resolved cathodoluminescence (CL) was used to investigate the spatial distribution of luminescence centers in CVD-grown diamond particles and polycrystalline films. For single particles grown at a low substrate temperature (nominally 650°C), one of the two most intense CL bands, the 2.156 eV band, was found to be associated with (111) facets. The CL image of the other intense band, the 2.85 eV band, showed considerable particle-to-particle variation among the same particles. The images of the 2.156 eV and 2.85 eV CL bands were found to have a complementary relationship for some particles. A model of competing recombination centers is proposed to help explain these results. Cross-sectional measurements of the CL spectra of polycrystalline films on silicon showed that the intensity of a silicon-impurity-related CL band decreases with increasing distance from the film-substrate interface. This depth variation is interpreted as due to a silicon impurity concentration gradient.
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CVD-GROWN DIAMOND PARTICLES AND FILMS

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ABSTRACT

Spatially and spectrally resolved cathodoluminescence (CL) was used to investigate the spatial distribution of luminescence centers in CVD-grown diamond particles and polycrystalline films. For single particles grown at a low substrate temperature (nominally 650° C), one of the two most intense CL bands, the 2.156 eV band, was found to be associated with (111) facets. The CL image of the other intense band, the 2.85 eV band, showed considerable particle-to-particle variation among the same particles. The images of the 2.156 eV and 2.85 eV CL bands were found to have a complementary relationship for some particles. A model of competing recombination centers is proposed to help explain these results. Cross-sectional measurements of the CL spectra of polycrystalline films on silicon showed that the intensity of a silicon-impurity-related CL band decreases with increasing distance from the film-substrate interface. This depth variation is interpreted as due to a silicon impurity concentration gradient.

1. INTRODUCTION

Luminescence spectroscopy is a useful method for defect characterization in diamond (1). Point defects (e.g., single-atom vacancy) and impurity atoms (e.g., nitrogen) are believed to be the primary constituents of the luminescence centers in diamond. Cathodoluminescence (CL) can be excited with high efficiency in diamond by a keV-range electron beam (2). Utilization of a scanning electron microscope (SEM) as the excitation source for CL allows the spatial distribution of the emission to be mapped with high resolution (3).

Results are presented here of a spatially and spectrally resolved CL study of diamond particles and polycrystalline films grown by hot-filament CVD. The CL from these specimens was found to consist of at least four distinct bands. Spectrally resolved images of the two most intense bands, at 2.156 eV and 2.85 eV, were obtained from diamond single particles grown at a nominal deposition temperature of 600° C. For these particles, the 2.156 eV band is associated with (111) facets, while the 2.85 eV band is associated in some cases with (100) facets and in other cases with (111) facets. In particles grown at a higher temperature, both bands are associated with (100) facets. These results are discussed in the context of a model of competing recombination
centers. Spatially resolved CL of diamond films on silicon substrates, viewed in cross-section, showed that the intensity of a silicon-impurity-related CL band decreases with increasing distance from the substrate. This behavior is attributed to a silicon impurity concentration gradient.

We previously presented CL imaging and spectroscopy results for CVD-grown diamond films and particles (4). In the previous work, only particles grown at a deposition temperature of 750° C were examined; in these particles, the CL arose primarily from (100) facets at all wavelengths. Other researchers have obtained similar CL imaging results for films grown by microwave-plasma CVD (5).

2. EXPERIMENTAL PROCEDURE

The diamond particles were grown in a tube-furnace hot-filament CVD reactor which has been described previously (6); the polycrystalline films were grown in a bell-jar hot filament CVD reactor. The following conditions were used for all depositions: gas mixture, 0.5% methane and 99.5% hydrogen; gas flow rate, 52 standard cm$^3$/min; pressure, 5x10$^3$ Pa; filament temperature, 1800° C; substrate, (100) oriented silicon. The particles were grown on as-received substrates which had a low density of diamond nucleation sites; the films were grown on diamond-polished substrates which had a higher diamond nucleation density. Particle depositions were carried out at nominal substrate temperatures of 600° C and 750° C; the films were deposited at 750° C. Because of filament heating, the true growth temperature is probably higher than the nominal temperature measured by a thermocouple placed beneath the substrate.

The experimental apparatus for CL imaging and spectroscopy in the SEM has been described previously (4). The electron-beam voltage for the CL measurements was 20 kV, and the electron-beam current was $-10^{-8}$ A. CL images with a spatial resolution of ~0.5 μm were recorded by a photomultiplier tube (PMT) with a wavelength range of 200 to 850 nm. Optical bandpass filters, with center wavelengths from 400 nm to 850 nm and full widths at half maximum of 40 nm, were used to obtain spectrally resolved CL images. CL spectra were measured by a 0.34 meter grating spectrograph that utilizes an intensified-photodiode-array multichannel detector and covers a wavelength range of 200 to 900 nm.

3. EXPERIMENTAL RESULTS

A typical CL spectrum from a particle deposited at 600° C, shown in Fig. 1, contains four distinguishable components, which are indicated in Fig. 1 by arrows. Three components give rise to sharp zero-phonon lines, at 1.68 eV, 2.156 eV, and 2.325 eV, as well as lower-energy phonon sidebands. The intense phonon sidebands of the 2.156 eV line are due to coupling to 0.045 eV and 0.085 eV acoustic phonons and to the 0.165 eV longitudinal optical phonon (7). The fourth component is a
broad, structureless band with maximum intensity at -2.85 eV.

The structures of the luminescence centers that give rise to these components have been tentatively identified by comparison to spectra reported in the literature (4). The 1.68 eV band is attributed to a center that contains a silicon impurity atom (8). The 2.156 eV and 2.325 eV bands are attributed to nitrogen-vacancy centers (centers that contain both a nitrogen atom and an atomic vacancy) with distinct structures (7),(9). The broad 2.85 eV band is attributed to a dislocation-related center, which may be either a donor-acceptor pair or an intrinsic state associated with dislocations (10).

The two most intense CL components, the 2.156 eV and 2.85 eV bands, can be selected by bandpass filters with center wavelengths of 600 nm and 450 nm respectively. The photon energy ranges of these filters are indicated by dashed lines in Fig. 1. For conciseness, spectrally resolved CL images obtained with the 600 nm and 450 nm filters will be referred to respectively as 600 nm and 450 nm images.

Spectrally resolved CL images and secondary-electron (SE) images of two particles grown at 600° C are shown in Fig. 2. One particle, shown in Fig. 2(a), has a cubo-octahedral form, and the other, shown in Fig. 2(b) has a pseudo-five-fold twinned form. The CL images appear blurred, compared to the SE images, because of electron beam spreading. According to semi-empirical models of electron scattering in solids, the penetration range of 20 keV electrons in diamond is ~2.8 μm, and the depth of greatest energy dissipation is ~1.4 μm (3),(11). The particles shown in Fig. 2 are ~20 μm in diameter; the CL is thus excited in the near-surface regions of these particles.

In the 600 nm image of the particle shown in Fig. 2(a), bright regions are associated with the centers or edges of triangular (111) facets, and dark regions are associated with the centers of square or octagonal (100) facets. In the 450 nm image, bright regions are associated with the centers of (100) facets. The two CL images shown in Fig. 2(a) are thus approximately complementary, bright regions in one image are correlated with dark regions in the other.

The 600 nm images of the two particles shown in Fig. 2 are similar; in both particles, bright regions are associated with (111) facets and dark regions are associated with (100) facets. Bright regions in the 450 nm image of the particle shown in Fig. 2(b) are, however, associated with (111) facets, in contrast to Fig. 2(a). The two spectrally resolved CL images in Fig. 2(b) are neither complementary nor identical to each other.

We have examined spectrally resolved CL images of other particles from the 600° C deposition, with results similar to those shown in Fig. 2; bright regions in the 600 nm images are always associated with (111) facets, while the location of bright regions in the 450 nm images varies from particle to particle. The variation of the 450 nm images does not
appear to be correlated in a consistent manner with the variation of the crystal growth habit (cubo-octahedral or five-fold twinned).

For particles deposited at 750° C, bright regions in both the 600 nm and 450 nm images are associated with (100) facets, and the two spectrally resolved images are very similar to each other. These results are in agreement with the results of previous studies by the present authors and by other researchers (4), (5).

The depth dependence of the CL in a continuous polycrystalline diamond film on a silicon substrate was investigated by breaking the specimen after deposition and examining it in cross-section. Two spatially resolved CL spectra, taken from near the top surface and the film-substrate interface of such a specimen, are shown in Fig. 3. These spectra are seen to contain the same features as the particle spectrum shown in Fig. 1. The primary difference between the two spectra is the relative intensity of the 1.68 eV band, which is several times greater in the spectrum taken near the film-substrate interface.

A number of spectra were taken from the cross-sectioned specimen to examine the depth dependence of the 1.68 eV band in more detail. In Fig. 4, two quantities are plotted as a function of distance from the film-substrate interface: the intensity ratio of the 1.68 band to the CL background in the same spectral region (which may arise from the low-energy tail of the 2.156 eV band), and the intensity of the CL background. The relative intensity of the 1.68 eV band decreases rapidly with increasing distance from the film-substrate interface, and is greatest when the electron beam is focussed on the substrate side of the interface. Because of its large penetration depth and lateral spreading, the electron beam can excite the diamond film when it is focussed on the silicon substrate near the interface (11).

4. DISCUSSION

We have developed a simple recombination model that can be used to relate the image contrast in the spectrally resolved CL images (Fig. 2) to the spatial distributions of the CL centers (12). The key assumptions are as follows: the initial step in the excitation of CL is electron-hole pair creation by the primary electron beam; several types of CL centers and non-radiative recombination centers compete for excitation by the free electron-hole pairs; the numbers of excited centers of each type are directly proportional to the number of free electron-hole pairs. The following equation may then be written for the CL intensity from centers of a particular type, labelled type (a).

\[ I_{CL(a)} = \frac{[n_a B a N_a]}{(\Sigma (B_i N_i) + \Sigma (b_j n_j))} \]  (1)

where \( N \) represents the concentration of CL centers of a particular type; \( B \) represents the rate for excitation of CL centers by electron-hole pairs; the subscript \( i \) represents a summation over all CL centers; \( n,b, \)
and j are the analogous quantities to N, B, and i for non-radiative centers; \( n_a \) is the luminescence efficiency of centers of type (a); and \( G_{eh} \) is the electron-hole pair generation rate. It is assumed that the concentrations N and n may vary from location to location within the specimen, but the other quantities in Eq. (1) are constant.

If there are only two dominant types of CL centers, labelled (a) and (b), and no non-radiative centers, then Eq. (1) simplifies to:

\[
I_{CL}(a) = \left[ \eta_a B_a N_a / (B_a N_a + B_b N_b) \right] G_{eh} 
\]

and a similar equation can be written for the type (b) centers. The sum of \( I_{CL}(a) \) and \( I_{CL}(b) \), weighted by the inverse quantum efficiencies, is then equal to \( G_{eh} \). In a region where \( I_{CL}(a) \) is higher than average, \( I_{CL}(b) \) is correspondingly lower. This argument implies that the images of the two dominant CL bands will be complementary to each other. The complementary relationship of the 2.156 eV and 2.85 eV CL bands observed for some particles [e.g., Fig. 2(a)] is explained by this case.

Suppose next that there are two dominant types of CL centers, but non-radiative centers are also present. Eq. (1) then has the form:

\[
I_{CL}(a) = \left[ \eta_a B_a N_a / (B_a N_a + B_b N_b + \sum B_j N_j) \right] G_{eh} .
\]

In this case, the sum of \( I_{CL}(a) \) and \( I_{CL}(b) \) is not constant, and the two images do not necessarily have a complementary relationship. According to the model, in specimens where the images of the two dominant CL bands are not complementary, non-radiative recombination must have a significant influence on the CL images. This appears to be the case for some of the particles grown at 600° C [e.g., Fig. 2(b)], and for all of the particles grown at 750° C. (Recall that the images of the two dominant CL bands are very similar for the latter).

According to Eq. (1), the ratio of the CL intensities from two types of centers, \( I_{CL}(a)/I_{CL}(b) \), is proportional to the ratio of concentrations, \( N_a/N_b \). The intensity ratio of the 1.68 eV band to the tail of the 2.156 eV band, plotted in Fig. 4, should thus represent the concentration ratio of 1.68 eV centers to 2.156 eV centers. Because the 1.68 eV centers are believed to contain silicon impurity atoms, the depth dependence shown in Fig. 4 may be due to a decrease in the concentration of silicon atoms with increasing distance from the silicon substrate. Such a silicon impurity concentration gradient might be due to diffusive transport of silicon atoms from the substrate into the film during the deposition process.

5. CONCLUSION

Spatially and spectrally resolved cathodoluminescence (CL) was used to investigate the spatial distribution of luminescence centers in CVD-grown diamond particles and polycrystalline films. For single
particles grown at a low substrate temperature (nominally 650° C), one of the two most intense CL bands, the 2.156 eV band, was found to be associated with [111] facets. The CL image of the other intense band, the 2.85 eV band, showed considerable particle-to-particle variation among the same particles. The images of the 2.156 eV and 2.85 eV CL bands were found to have a complementary relationship for some particles. A model of competing recombination centers is proposed to help explain these results. Cross-sectional measurements of the CL spectra of polycrystalline films on silicon showed that the intensity of a silicon-impurity-related CL band decreases with increasing distance from the film-substrate interface. This depth variation is interpreted as due to a silicon impurity concentration gradient.

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Fig. 1. CL spectrum of a diamond single particle grown at 600° C. The four indicated spectral features are attributed to a silicon impurity center (1.68 eV zero-phonon line) two types of nitrogen-vacancy centers (2.156 eV and 2.325 eV zero-phonon lines), and a dislocation-related defect (2.85 eV band). Dashed lines indicate the ranges for the 600 nm and 450 nm CL images.

Fig. 3. Spatially resolved CL spectra of polycrystalline diamond film on silicon viewed in cross-section, taken from (a) near film-substrate interface, (b) near top surface.

Fig. 4. Intensity ratio of 1.68 eV CL band to spectral background (squares), and intensity of background (circles), as function of distance from film-substrate interface. Locations of interface and top surface of film are indicated by dashed lines.
Fig. 2. Secondary-electron (SE) and spectrally resolved CL images of two diamond particles grown at 600°C. Two spectrally resolved CL images, taken with 600 nm and 450 nm bandpass filters, are shown for each particle. (a) Particle with cubo-octahedral habit. (b) Particle with pseudo-five-fold twinned habit.
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