Technical Report

Imaging of Defects in IIa Diamond by Cathodoluminescence Field Emission Scanning Electron Microscope

S. Awata, H. Matsuo, Y. Kimura*, Y. Takai* and R. Shimizu

*Department of Applied Physics and *Department of Material and Life Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

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Abstract

A cathodoluminescence-Field Emission Electron Microscope equipped with a newly developed scanning system for photon counting was applied to cathodoluminescence (CL) imaging of defects in high pressure synthesized high purity IIa diamond. The CL-imaging for the emission lines of free-exciton (λ=235nm, E=5.27eV) and band-A (λ=425nm, E=2.92eV) has enabled us to observe those defects that exist deeper inside beneath the surface.

1. Introduction

Cathodoluminescence scanning electron microscope (CL-SEM) [1, 2] has recently become a powerful tool for characterization of, particularly, those semiconductors having wide band gaps, for which photo cathodoluminescence is no more useful. In fact, CL-SEM has been intensively used for characterizing synthesized diamonds, the spectral range of which is covered by the luminescence band extending from 1.2eV (near infrared) to 5.3eV (λ = 235nm, ultraviolet). Since these CL-SEM's are, from the instrumentation point of view, equipped with a thermoionic cathode electron gun, it has been often pointed out that the light emitted from the cathode significantly deteriorates the signal to noise ratio (S/N). To solve this problem a primary beam of high current intensity ~1μA has been used to ensure sufficient S/N, enabling CL-mapping to be performed in the current mode. However, electron beam irradiation of high current intensify does incur serious surface contamination and radiation damage.

The advantage of the use of the field emission (FE) SEM is no interference from light from the cathode since it is operated at room temperature, ensuring high S/N even with an electron beam of such low current intensity as ~1nA. Because of this, therefore, the FE-SEM with photon counting system has recently been attracting much attention. However, the observation of CL mapping images of specimens with the FE-SEM has not yet been reported because a specific device is needed to realize CL-mapping by photon counting system.

This paper reports the first observation of CL-mapping image under the CL-FESEM [3], in which a scanning system for photon counting has been newly developed. This has allowed us to observe the defects in a high pressure synthesized high purity IIa diamond using a primary beam intensity of 1nA. The CL-images of free-exciton (λ=235nm, E=5.27eV) and band-A (λ=425nm, E=2.92eV) emissions from the diamond have clearly revealed the defects which could not be observed by convention secondary electron image.

2. Experimental

The CL-FESEM was operated at 25kV with a probe size of, ~100nm in diameter, and current intensity, 1nA, three order of magnitude lower than those of conventional CL-SEM's. For CL-mapping the signals (photons) from each pixel are photon-counted for 50ms. Scanning of the electron probe over a specimen surface was synchronized with a programmable scan-coil controlled by a personal computer. The CL-image observations were performed with 128x128 pixels at an observation time of ~800sec by keeping a specimen at a temperature between 80 and 85K. The specimen was a high pressure synthesized high purity IIa diamond.

3. Results and Discussion

Fig. 1 shows CL-mapping images and emission spectra of the high pressure synthesized high purity IIa diamond. The photographs (a) are the secondary electron images obtained at different magnifications. The mapping (b) was imaged with the signal of free-exciton emission (λ=235 ±2nm) and the image (c) with the band-A emission (λ=425 ±2nm). Relevant cathodoluminescence spectra from the different local areas (d & e) are also presented in the figure. Note that the secondary electron images (a, ×80) has revealed a very fine crack-line running across the middle of the specimen. This crack-line was observed as a dark line of very low contrast in the image (b, ×80) and as a line of small bright spots in the image (c, ×80), demonstrating that defects and/or impurities are localized along the crack-line. Looking at the brightest spot in the image (c, ×80) no trace of defects could be observed in the SEM-images (a), suggesting that the defects do not exist. It may be also worthwhile noting that a dark-line exists in the middle of this bright spot (c, ×400 & ×2000) and a bright area is observed around the dark-line. It has been reported that the free-exciton emission (λ = 235nm) is very sensitive to the crystallinity [4]. The rather wide dark-line area observed in the images (b, ×400 & ×2000) corresponding to the dark-line of the images (c), therefore, should be due to crystal defects. The bright area around the dark-line in the image (c, ×400 & ×2000) is probably due to impurities localized around the crystal defects, leading to generation of band-A emission, because the band-A emission is closely related to the impurities and/or crystal defects [5].

Consequently, the CL-FESEM equipped with scanning system for photon counting has led to successful observation of CL-images of free-exciton emission under irradiation of primary beam of very low current intensity of 1nA. This low current intensity has enabled observation of a specimen surface without significant surface contamination which deteriorates considerably the S/N for the signals of ultraviolet region.

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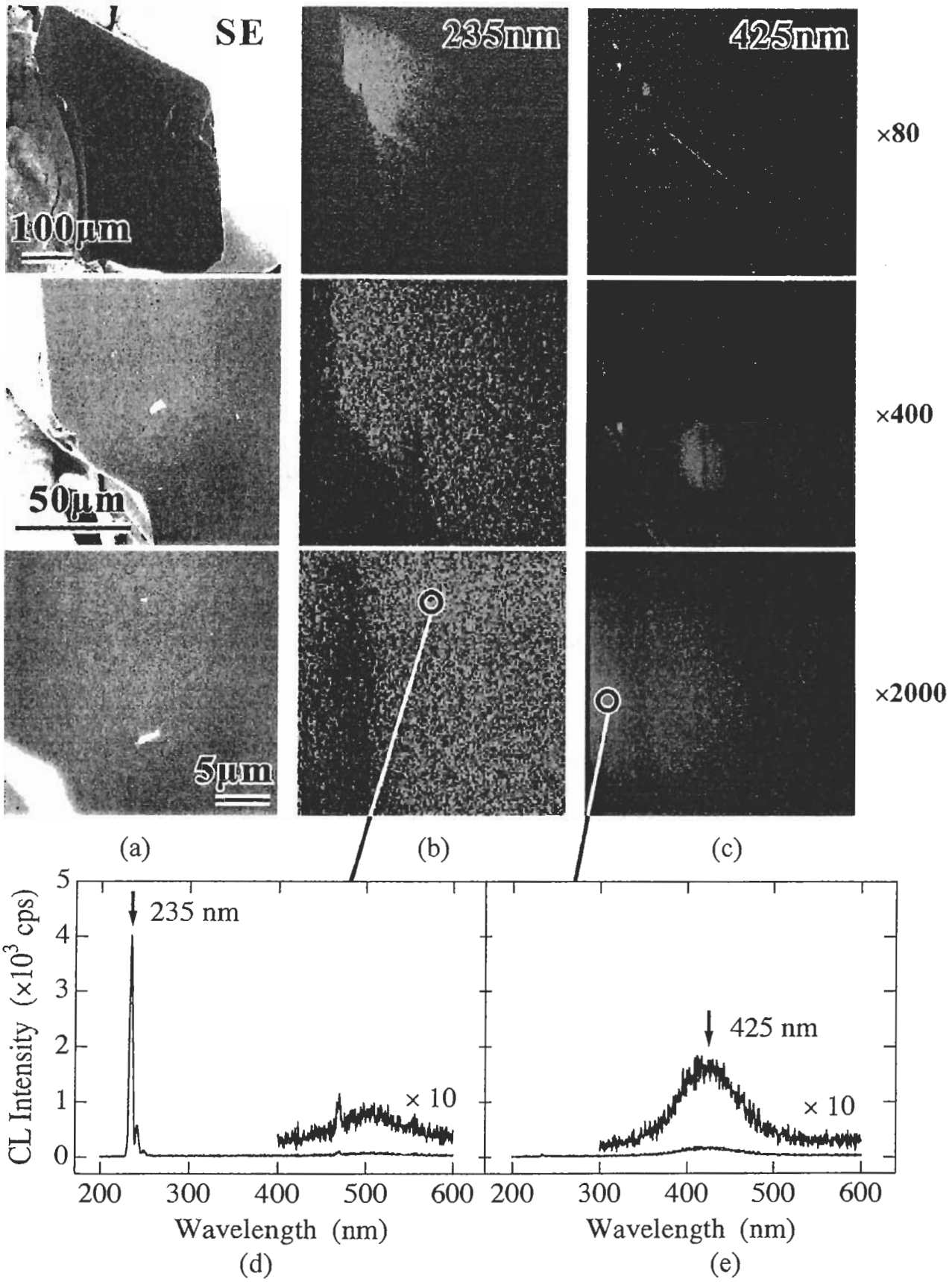

Fig. 1 Scanning images of a high pressure synthesized high purity IIa diamond with secondary electrons (a) and cathodoluminescence of free-exciton emission (λ=235nm) (b) and band-A emission (λ=425nm) (c) at different magnifications. Relevant spectra from different local areas are depicted in (d) and (e).

Q&A

Reviewers:

Y. Fukuda (Shizuoka Univ.)

M. Suzuki (NTT-AT)

Q1:

What type of defects are the origins of the band-A transitions? Are they the defects in electronic state? What is the significant achievement of the newly developed system, which has enabled an image mapping.

A1:

It has been empirically recognized that existence of crystallographic defects and impurities is essential to the band-A transition. In fact photoluminescence has long been used, over half century, for assessment of crystallinity of diamond. Its basic mechanism, however, has not been well understood.

In this test we have briefly mentioned this situation by referring to the papers. With respect to the band-A transition, it has hardly been discussed, to our knowledge. Cathodoluminescence mapping image allows us directly to observe the localization of defects. Particularly, high magnification observation will be very useful for this purpose.

Q2:

Isn't the diamond insulator? If so did you devise to prevent the specimen from being charged up?

A2:

A high quality natural diamond is exactly a very good insulator. Synthesized diamonds are not insulator but known to be semiconductor which does not require any treatment such as coating etc. for ordinary SEM observation.

Q3

Are the information depth's of SE- and CL-signals the same order of magnitude?

A3

No, they are quite different. The information depth of CL-signals is extending over its range of incident electrons, nearly micron, whereas that of SEM is known as several nanometers.