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# Ultraviolet random lasing from a diamond nanoparticle film

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We demonstrated ultraviolet random lasing from a diamond nanoparticle film, in which commercially available diamond nanoparticles with an average size of 25 nm acted as the gain medium and scatterers. By optically exciting the diamond nanoparticle film at an excitation wavelength of 355 nm, discrete sharp peaks, superposed on a collapsed broad emission spectrum, randomly appeared at wavelengths around the broad emission maximum (~382 nm) when the excitation intensity exceeded the threshold. From the dependence of lasing peak intensities measured at different locations as a function of excitation intensity, the threshold was estimated to be approximately several tens of MW/cm$^2$. © *2014 AIP Publishing LLC*.
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Diamond is an attractive material for applications as light sources and semiconductor power devices because of its excellent physical properties, i.e., high thermal conductivity, high carrier mobility, various color centers, and high breakdown field strength.[1,2] Because diamond has a wide band gap (5.48 eV) and is transparent with a high refractive index, it can be used as a deep ultraviolet (DUV)/ultraviolet (UV) light source for sterilization and cleaning, medical applications, high density recording, and a high color-rendering white light source. However, its application as a laser light source still remains challenging.

On the other hand, random lasers, which are composed of randomly distributed scatterers and gain materials, have recently attracted attention as unique laser sources without clear cavity structures.[3–13] Random lasers can be easily fabricated, for instance, by nanoparticle assembly, because disorder plays an important role in randomly distributed feedback because of the interference effects of recurrent multiple scattered light.[14–21] Therefore, we expected to realize an easily fabricated and low-cost random laser with diamond nanoparticles as scatterers and gain medium utilizing excellent properties of these nanoparticles, such as various color centers, wide bad gap, and high refractive index. In this paper, we demonstrated UV random lasing from a diamond nanoparticle film, in which we succeeded to observe the nonlinear evolution of discrete sharp peaks randomly appeared at the wavelengths around the broad emission maximum (~382 nm) when the excitation intensity exceeded their threshold.

Commercially available monocrystalline synthetic diamond nanoparticles (Microdiamant AG, MSY 0–0.05, mean diameter = 25 nm) were used as scatterers and gain medium. To remove the sp$^2$ layer on the diamond nanoparticles, they were sintered at 425 °C in air for 5 h, according to the process described by Osswald *et al.*[22] After the sintering, the color of the diamond nanoparticles changed from black to yellow. The nanoparticles were then dispersed in a hexane solution and a drop of this solution was put on a cover glass and dried. The sample was fixed on a microscope stage and pulses from a Q-switched pulsed laser (355 nm, 100 ps, 1 kHz) were irradiated on the sample by an objective lens (10×, NA = 0.5, spot size ~ 200 $\mu$m). Emission from the diamond nanoparticle film was collected through the same objective lens and passed through a pinhole (about 35 $\mu$m on the sample plane). The emission was then detected by a spectroscope equipped with a cooled charge-coupled device (CCD) camera, and the emission spectra were measured with varying the excitation intensity at arbitrary sample positions. The insets in Fig. 1 show emission images from the diamond nanoparticle film. Over most of the film, we observed green–red broad emission and no distinct blue emission (Fig. 1(a)). When scanning with constant excitation intensity, we occasionally observed spots with intense blue emission within the broad excitation area, and their emission spectra showed an intense peak at around 380 nm (Fig. 1(b)). Note that the blue emission spots could be observed in the film after sintering, but it was difficult to find blue emission spots in the film before sintering.

Among these blue emission spots, there were certain spots with higher emission intensities, which were clearly different from the normal blue spots (inset in Fig. 2(a)). Figure 2(a) shows the emission spectra from one of the intense blue spots for excitation intensities of 40, 77, and 95 MW/cm$^2$. As the excitation intensity increased, we observed that discrete sharp peaks, superposed on the collapsed broad emission spectrum, randomly appeared at

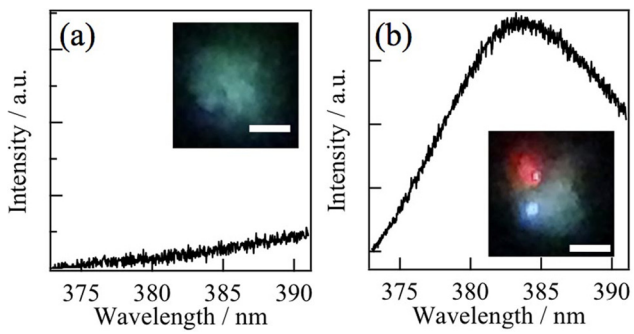


FIG. 1. Emission spectra at different spots within a diamond nanoparticle film. Insets show CCD images of emissions. The excitation intensity was kept constant, and the white bars indicate the scale of 50 $\mu$m.

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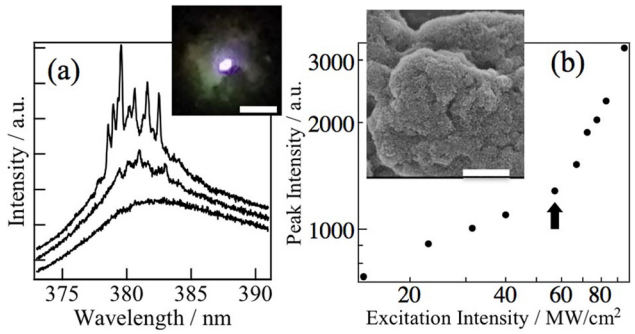


FIG. 2. (a) Emission spectra measured at an intense blue spot in a diamond nanoparticle film. The excitation intensities were 40, 77, and 95 MW/cm$^2$ from bottom to top. The inset shows the CCD image of the UV random lasing. (b) Emission peak intensity vs. excitation intensity. The horizontal axis for excitation intensity is logarithmically plotted, and an arrow indicates the threshold intensity. The inset shows the SEM image of diamond nanoparticles. White bars indicate the sizes of 50 $\mu$m in (a) and 1 $\mu$m in (b).

wavelengths around 380 nm. Figure 2(b) shows the logarithmic plots of the peak intensity vs. the excitation intensity. From the results, we confirmed the nonlinear evolution of the emission peak intensity when the excitation intensity exceeded the threshold (about 60 MW/cm$^2$). In addition, the observed relative peak intensities changed depending on the excitation intensity and each shot of the excitation pulse.

We have to note that because diamond nanoparticles have a mean diameter of 25 nm, it is too small compared to the excitation and emission wavelengths. Therefore, it would be strange that we observed random lasing with discrete sharp peaks from the diamond nanoparticle film, because the scattering strength of individual nanoparticles should be so small to derive the random coherent feedback. To clarify this, we measured a scanning electron microscope (SEM) image and also coherent backscattering of diamond nanoparticles. The inset in Fig. 2(b) shows a SEM image of the sample. From the image, we found that the aggregation of diamond nanoparticles occurred and the film had a rough structure, which scale was enough larger than the wavelengths. In addition, from the measurement of coherent backscattering, the mean free path of the diamond nanoparticle film was roughly estimated to be about 11 times of the wavelength. Thus, we thought that the particle aggregation would play an important role for inducing random laser in the diamond nanoparticle film.

We observed the same phenomena for different sample sites and different films. Figure 3 shows the emission spectra for 4 different sites on the film. The peaks were always at ~380 nm. Figure 4 shows the scatter plot of lasing peak wavelengths and thresholds for different sample sites and different films (circles), and the gray line indicates the spontaneous emission spectrum from a blue spot in the diamond nanoparticle film for excitation below the threshold. The discrete sharp peaks clearly concentrated around the peak wavelength of the spontaneous emission, whereas their thresholds were dispersed from several tens to several hundred MW/cm$^2$. These results suggested that because of randomness, laser oscillation initiated at a wavelength with strong gain. The difference in the thresholds reflected the difference in the surrounding conditions at each location. Because these behaviors were similar to those of conventional

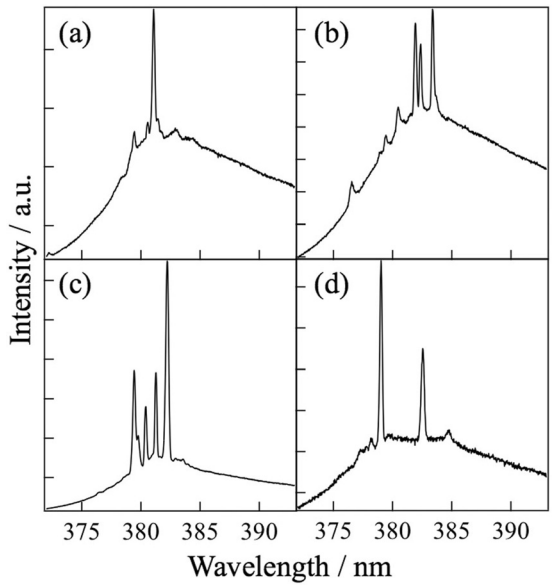


FIG. 3. (a)–(d) Emission spectra measured at different sites on the diamond nanoparticle film.

random lasers, we concluded that UV random lasing was induced in these diamond nanoparticle films.

As a laser device using diamonds, many studies of Raman lasers have mainly been reported.[23,24] However, because our observed lasing peaks were different from the typical reported Raman peaks (1333 cm$^{-1}$ and 1600 cm$^{-1}$), and different wavelengths were observed at different observation spots, we thought that Raman lasing was not the origin of the nonlinear evolution of the observed sharp peaks. Gorelik and Rakhmatullaev have reported fluorescence around 380 nm from diamond powder with a spectral shape similar to our emission spectra when the excitation intensity is below threshold; they attributed this fluorescence to the N2 defect.[25] Furthermore, from previous studies[26,27] in which the sp$^2$ layer on the surface of diamond nanoparticles suppressed emission from the diamonds, we thought that the surface conditions of diamond nanoparticles would play an important role in UV random lasing. In fact, by comparing the nanoparticle film before and after sintering, intense blue spots and UV lasing were rarely observed before sintering,

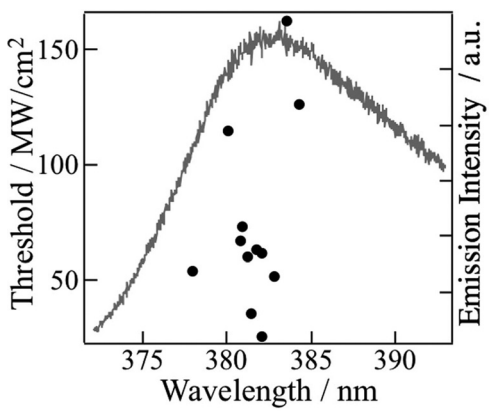


FIG. 4. Scatter plots of threshold intensity vs. lasing wavelengths (solid circles). The gray line indicates the spontaneous emission spectrum of a diamond nanoparticle film when the excitation intensity was lower than the threshold.

whereas they were easily observed after sintering. In addition, we thought that because of the removal of $sp^2$ layers due to annealing, surface carbon layers could not be the origin of the UV emission. On the basis of these results, we conjectured that before sintering, lasing is less likely because of emission suppression by the $sp^2$ layers on the diamond surface. Whereas after sintering, N2 defect emission would increase because of the removal of the $sp^2$ layer, resulting in an increase in UV random lasing. Therefore, we expect that optimization of the temperature and ambient nitrogen concentration during annealing could increase the probability of UV random lasing in a diamond nanoparticle film.

In summary, we demonstrated random lasing from a diamond nanoparticle film. We observed nonlinear evolution of discrete sharp peaks at wavelengths around 380 nm, a wavelength never before observed for diamond laser oscillation. Even though further investigation is necessary to understand the mechanism for the observed random lasing, considering the excellent properties of diamonds, our demonstration of random laser oscillation in diamond nanoparticle films in the UV region (~380 nm) suggests excellent promise for future diamond-based devices.

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