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研究成果の概要（和文）：低密度Znドープ窒化ガリウムの量子井戸サンプル作成、光学評価を行った。このZnドープGaNから、２．６eV~2.7eV付近のエネルギー（～４７０nm）で今まで発表されていなかった鋭い発光ピークを測定することができた（発光線幅は2meV程度）。発光線の原因は未確認ですが、Zn：N状態であると考えられる。発光は安定する（秒スケールのスペクトル拡散などはほとんど無い）が、低温(<50K)のみで現れ、フォノンとの相互作用は強い。単一光子発生を確認するために自己相関g(2)関数を測定したが、アンチバンチングはでない。

研究成果の学術的意義や社会的意義
The basic understanding of semiconductors is crucial for the development of many devices such as LEDs, Lasers, and single photon emitters. In this research we have shown that Zn doping of GaN can allow for a new, hitherto unreported, emission line, and investigated its optical properties.

研究成果の概要（英文）：low density Zn doped GaN quantum wells were fabricated and investigated with optical spectroscopy. Hitherto unreported emission lines in the blue at ~2.6~2.7eV (~470nm) were observed and thoroughly investigated. Although we could not confirm the exact origin of the emission lines, it is anticipated that they originate from Zn replacing N sites in the host GaN crystal. The emission lines are stable (exhibiting almost no spectral diffusion on second time scales), but they only seem to appear at low temperatures (<50K), and exhibit strong phonon interactions. At present single photon emission could not be obtained from these emission centers.

研究分野：quantum materials

キーワード：semiconductor　optics

１．研究開始当初の背景

Semiconductors are widely used in various light emitting technologies such as LEDs and Lasers, and are being investigated for the development of quantum, single photon, emitters in laboratories around the world. Single photon emitters are expected to be a key element for the development of quantum information processing, and are thus of significant interest.[1] The III-Nitride material system is being heavily studied for such emitters as it can be used to generate light at several wavelengths (in principle ranging from the ultraviolet to the infrared) depending on the exact material composition,[2] and the species of impurities that exist in the crystal. Zinc is one such impurity that was trialed as a p-type dopant in GaN (to assist with electrical injected device fabrication), and was also shown to form several deep acceptor levels, sometimes replacing Ga,[3] and sometimes replacing N,[4] leading to bright emission over a range of wavelengths at the blue end of the spectrum.[5] Although Magnesium has largely replaced Zinc as the p-dopant of choice for III-nitride LEDs and laser diodes, there is still much to study about Zn-doped GaN, and to see if single photon emission is possible via the isolation of individual emission centers.[6]

２．研究の目的

The aim of this project was to further elucidate the optical properties of Zn-doped GaN. In particular, by producing low density samples the broad aim was to try and isolate an individual Zn based emitter for single photon emission.

３．研究の方法

In order to isolate an individual emitter, it is necessary to fabricate a sample with a low density of optically active Zn atoms. Metal Organic Chemical Vapour Deposition (MOCVD) was used for sample growth with TMG, TMA, HH_3, and DEZ as sources of Ga, Al, N, and Zn, respectively. The main approach employed during this research project was the use of a growth memory effect, in which a dummy sample of Zn doped GaN was fabricated, followed by the growth of a nominally un-doped sample. The remaining zinc atoms in the reactor chamber after the dummy growth run are absorbed into the crystal during the main sample growth, resulting in a low density Zn-doped sample. Due to the low density of Zn dopants it would not be possible to measure the density using techniques such as Secondary Ion Mass Spectroscopy (SIMS), but we estimate that the doping density is lower than $<10^{14}$ cm^{-3}. In order to further increase our chance of isolating an individual emitter, we fabricated $Al_{0.11}Ga_{0.89}N$/GaN quantum well structures, such that we could selectively excite a limited region of the sample (for example by selectively exciting carriers into the quantum well by using an excitation energy below the $Al_{0.11}Ga_{0.89}N$ bandgap). The main experimental method used for optical characterization was micro-photoluminescence spectroscopy. The samples were held under vacuum in a closed cycle liquid helium cryostat such that the sample temperature could be controlled between ~4K and 300K. The samples were excited using a series of continuous wave lasers (λ= 325nm, 355nm, 375nm, 405nm), or pulsed laser (wavelength tunable, 80MHz). Spectroscopy was performed using a 30cm grating spectrometer equipped with a nitrogen-cooled charge coupled device (CCD). Emission statistics (to test for the emission of single photons) could be measured using a Hanbury-Brown & Twiss setup

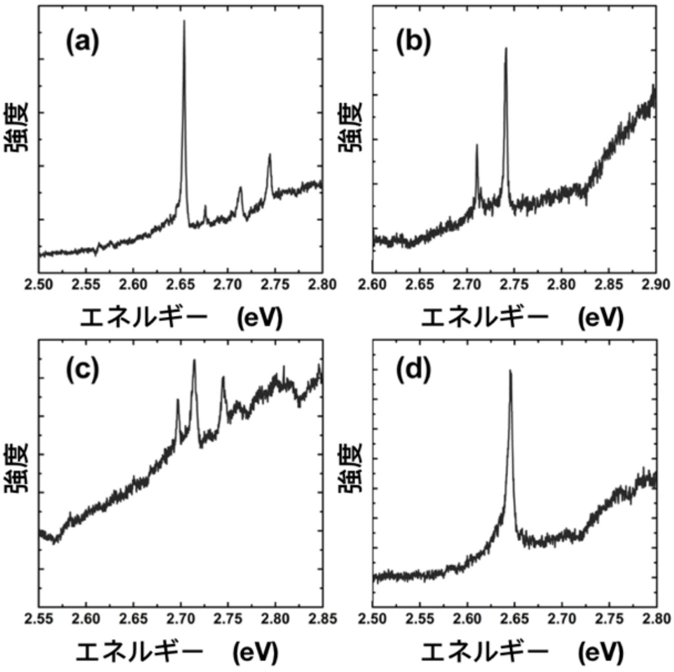

Figure 1. Examples of emission peaks observed from Zn doped GaN quantum wells. Excitation conditions are a) 355 nm CW excitation at 120μW, b) 355nm CW excitation at 48μW, c) 325nm CW excitation at 160μW, d) 355nm CW excitation at 48 μW.

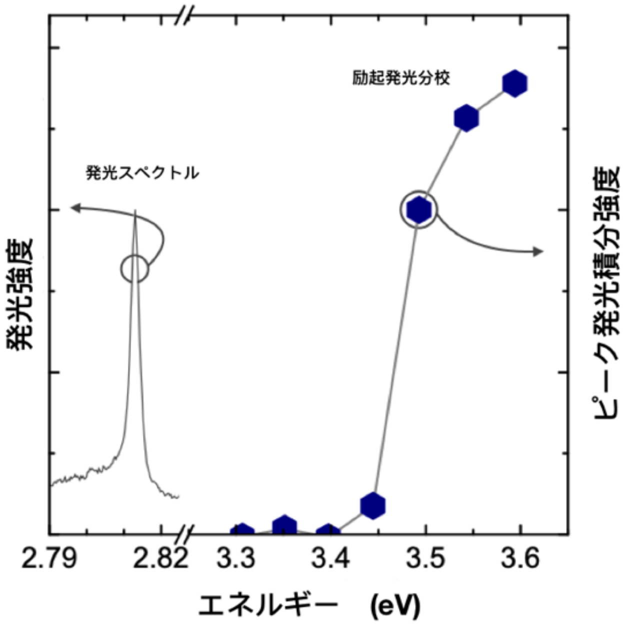

Figure 2. PLE spectrum of an individual emission peak. The peak is not observed for excitation below the GaN bandgap (~3.5eV).

consisting of two photomultiplier tube detectors and a beamsplitter (the spectrometer is used as a tunable spectral filter in order to isolate the emission during this measurement).

４．研究成果

Fabrication of the samples was performed as outlined in the previous section, and optical characterization was performed at low temperatures (~6K) in order to suppress the effects of phonon interactions. Zinc incorporation into the host crystal was confirmed by the presence of a broad emission in the blue region of the spectrum. However, sample mapping revealed the existence of spatially isolated regions where emission peaks could be identified. The emission peaks (as shown in figure 1) could be found typically in the low energy tail of the broad emission background. The peaks have reasonably low linewidths (~2meV), and appear to have acoustic phonon side bands on the low energy side. To the best of our knowledge this is the first time that such emission peaks have been observed in Zn-doped GaN. The observation in this case is likely due to the low density nature of the Zn-doping. We note that the emission linewidths are on the same order as those measured from established GaN related quantum emitters, such as single photon emitting AlGaN/GaN Quantum Dots.

We proceeded to investigate several emission properties of the emission peaks. The excitation process of the emission lines was investigated using photoluminescence excitation (PLE) spectroscopy. As can be seen in in figure 2, the emission intensity of the peaks drops rapidly for excitation below ~3.5eV, corresponding to the GaN bandgap. This is important as it supports the notion that the Zn states are not excited directly, but instead become occupied by carriers that are first excited into the GaN quantum well and then diffuse to the emission centers.

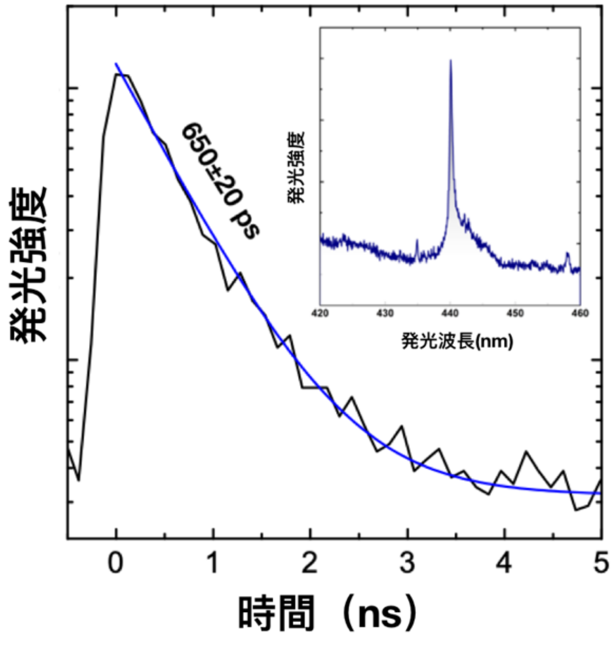

Figure 3. Emission lifetime of single Zn-related emission peak. The lifetime is measured to be 650ps in this case.

Next, the emission lifetimes of the emitters were measured using time resolved photoluminescence spectroscopy (TRPL). Pulsed excitation at a wavelength of 355nm was used for this experiment, and sub-nanosecond lifetimes of a few hundred picoseconds were measured (see figure 3). This fast lifetime is likely dominated by non-radiative processes (see below).

In order to gain more information on the emission properties, the temperature dependence of an emission line was investigated thoroughly (see figure 4). It is clear that the emission rapidly decreases in intensity as the temperature is raised, and we found it difficult to observe emission above temperatures of ~50K. This indicates that the charge carriers giving rise to the emission are weakly confined. In fact, as the emission rapidly

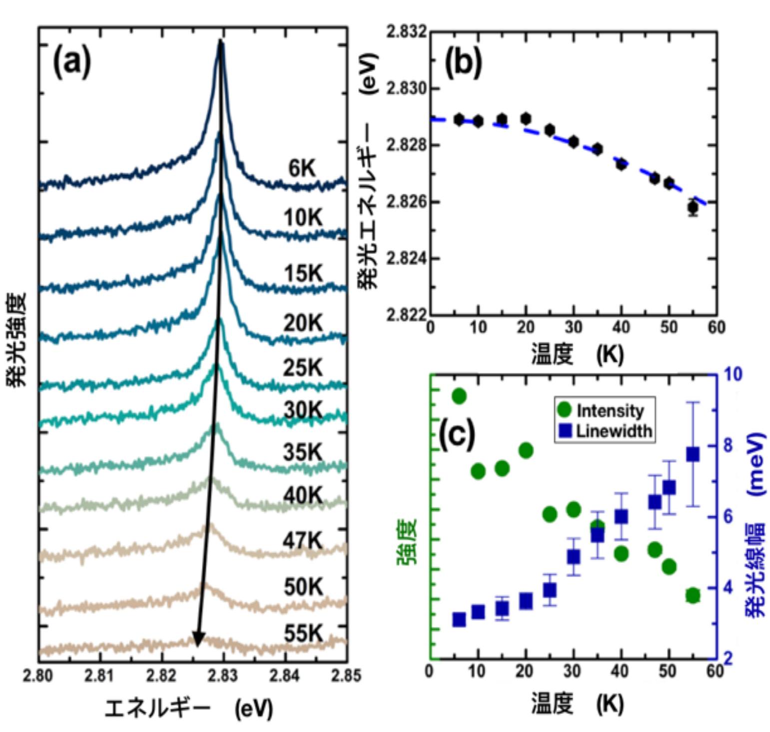

Figure 4. Temperature dependent emission properties of a Zn related emission line. (a) Emission spectra at various temperatures. (b) The temperature induced shift of the emission energy. (c) Emission linewidth and integrated intensity.

quenches with increasing temperatures, we believe that significant non-radiative recombination is occurring even at low temperature (which could also explain the fast emission lifetimes). The emission line also broadens significantly with increased temperature, indicating a strong acoustic phonon interaction (the more or less linear increase of the linewidth with temperature is consistent with previous reports on acoustic phonon related emission broadening). The linewidth broadening occurs at a rate of ~0.15meVK^{-1}, which is similar to some reports from GaN QDs, albeit occurring at much lower temperatures in this case.[7] These properties (strong phonon broadening, and rapid emission quenching) are possible reasons for the fact that these emission lines have not previously been observed or reported. In addition to the linewidth broadening, the emission exhibits a clear redshift with increasing temperature, which is well described by the Varshni equation with typically used GaN parameters: $E(T) = E_0 - \alpha T^2/(T + \beta)$ with $\alpha =$ 0.59meV/K and $\beta =$ 600K.[8]

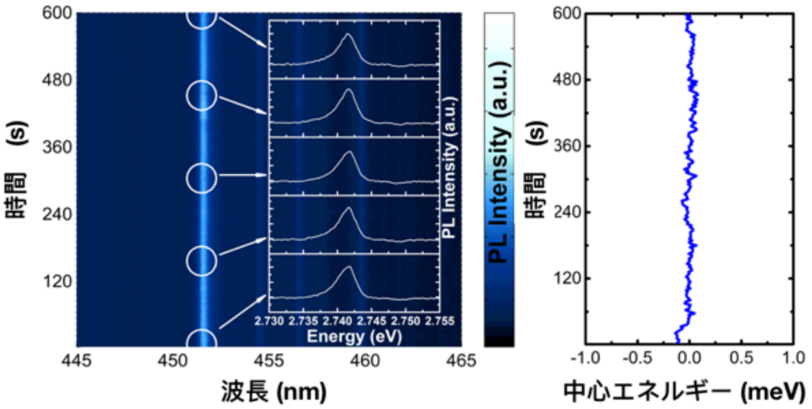

Figure 5. Emission stability measurements. The left panel shows a map of the emission spectra accumulated over a period of 10 minutes. Only very minor fluctuations are observed. The right panel shows a plot of the extracted peak center over the 10 minute period. The fluctuations are smaller than the resolution limit of the experiment.

The stability of the emission was also measured. Emission centers in III-nitrides typically exhibit a pronounced spectral diffusion, whereas it is clear that the emission lines measured here are very stable. We measured an emission spectrum of one emission line over a period of 10 minutes, and observed only minor fluctuations in the emission energy over time (see figure 5). The *x*-axis of the right panel in figure 5 is less than the full width of the emission peak, indicating the scale of the minor fluctuations (in this case lower than the spectral resolution of the experimental setup).

Autocorrelation experiments were performed on the emitters in order to evaluate the photon statistics of the emission via measurements of $g^{(2)}(0)$. At this stage, single photon emission could not be confirmed, and no antibunching in the $g^{(2)}(\tau)$ measurement could be observed. One possible reason for this could be significant background in the emission spectra, as is apparent in figure 1. In an attempt to suppress this background, and further isolate the emission from an individual emitter, a thin layer of aluminium was deposited on the sample surface and small apertures were formed using electron beam lithography (see figure 6). These apertures will allow light through, and the surrounding aluminium will block emission that does not originate from the area under the aperture. Such masks were fabricated in bulk on the sample surface, with a range of openings from around 300nm to 2μm in size. The masked samples were also investigated and mapped, and although emission with a lower background could be attained, single photon emission was not detected.

Considering the origins of the observed emission peaks, it is believed that they are related to Zn_N states, with possible local variations in emission energy due to local fluctuations in internal electric field in the quantum well (possibly induced by the presence of the Zn, or fluctuations in the barrier composition or well thickness). Further investigation, including theoretical simulations, will be required to elucidate the nature of the emitters.

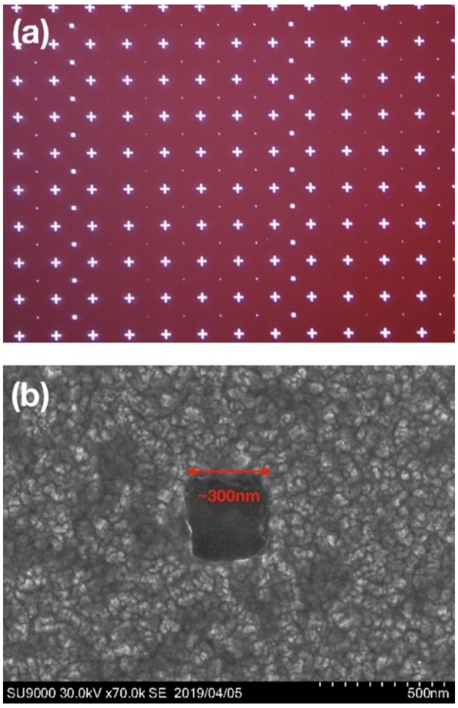

Figure 6. Aluminium masks fabricated on a Zn-doped AlGaN/GaN quantum well sample. (a) Optical microscope image (back illuminated) showing the apertures and cross shaped markers. (b) Scanning electron microscope (SEM) image of a single aperture

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５．主な発表論文等

〔雑誌論文〕（計１件）
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