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Ultraviolet Lasing from Vertically-Aligned ZnO Nanowall Array

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***Abstract*—**Zinc oxide (ZnO) is one of the light emitting materials in ultraviolet (UV) region. In addition, ZnO nanostructures are also attracting increasing research interest as building blocks for UV optoelectronic applications. We have succeeded in synthesizing vertically-aligned ZnO nanostructures by laser interference patterning, which is catalyst-free and non-contact technique. In this study, vertically-aligned ZnO nanowall arrays were synthesized using two-beam interference. The maximum height and average thickness of the ZnO nanowalls were about 4.5 μm and 200 nm, respectively. UV lasing from a piece of the ZnO nanowall was obtained under the third harmonic of a Q-switched Nd:YAG laser excitation, and the estimated threshold power density for lasing was about 150 kW/cm^2. Furthermore, UV lasing from the vertically-aligned ZnO nanowall was also achieved. The results indicate that ZnO nanowalls can be applied to random laser.

***Keywords*—**Zinc Oxide, nanowall, interference laser, UV lasing

I. Introduction

ZINC oxide (ZnO) is a group II-VI semiconductor with a wide band gap energy of 3.37 eV and a large exciton binding energy of 60 meV [1], which is larger than the thermal energy at room temperature. Thus, ZnO is expected as a promising material for optoelectronic devices in UV region. In addition, ZnO nanostructures, such as nanowires, nanorods, have attracted a great deal of attention because of their unique optoelectronic properties. ZnO nanostructure-based light emitting devices, including light emitting diodes (LEDs) [2]-[4] and UV lasing mediums [5], [6] have been reported. Those ZnO nanostructures can be fabricated by several methods, such as chemical vapor deposition (CVD) [7], hydrothermal synthesis [8]; nanoparticle assisted pulsed laser deposition (NAPLD) method [9], [10] and so on. However, in order to apply the ZnO nanostructures to practical devices, controlling growth position is essentially required. In general, lithographic and imprinting methods are often introduced [11]-[14]. On the other hand, these manufacturing processes are complex and catalysts or resists are generally used. In contrast, we have succeeded in growing periodic ZnO nanostructures by laser interference patterning to a ZnO buffer layer [15], [16]. In this study, we synthesized vertically-aligned ZnO nanowall array by using two-beam interference. The structural and optical characteristics of the ZnO nanowall array are reported.

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II. Synthesis of ZnO Nanowalls

ZnO nanostructures were fabricated on buffer layer on *a*-cut sapphire substrates by NAPLD method [15], [16]. Before the growth of the ZnO nanostructures, the buffer layer for position control was prepared by the pulsed laser deposition (PLD) method using ZnO sintered target. The *a*-cut sapphire substrate, which was placed on a SiC plate in front of target, was heated at 500°C. These were placed in a vacuum chamber filled with O_2 gas at 3 Pa. Target was ablated for 10 min with the third harmonics of a Q-switched Nd: YAG laser (λ = 355 nm) with a repetition rate of 10 Hz at a fluence of 1.5 J/cm^2. A thickness of the ZnO buffer layer was about 100 nm. Subsequently, two-beam laser interference patterning was performed to the buffer layer using the third harmonics of a Nd:YAG laser (355 nm) to the buffer layer with a fluence of 3.0 mJ/cm^2. Fig. 1 shows the schematic of the two-beam laser interference patterning. The laser beam was diffracted by a grating, and diffracted beams were collimated by lens no.1. Then, only two beams were extracted by a spatial filter, and they were focused on the surface of ZnO buffer layer by lens no.2.

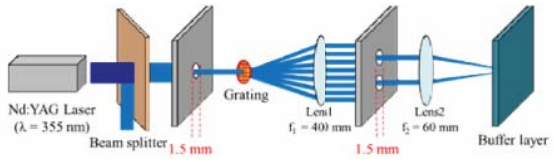

Fig. 1 Schematic of two-beam laser interference patterning

Figs. 2 (a) and (b) show the scanning electron microcopy (SEM) image and cross-sectional profile of the patterned buffer layer measured by the atomic force microscope (AFM). The periodic structures were obtained in a single shot laser patterning. The patterned depth of ZnO buffer layer was about 86 nm, and the rims were created at the edge of each irradiated line.

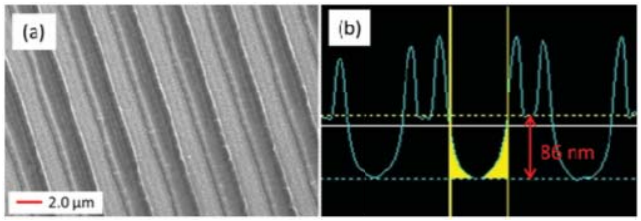

Fig. 2 (a) SEM image of the patterned ZnO buffer layer, and (b) cross-sectional profile of the patterned buffer layer measured by AFM

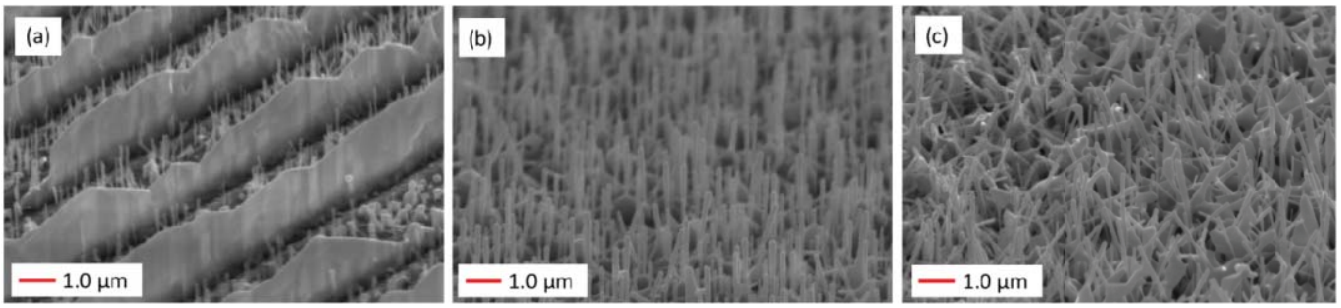

Fig. 3 SEM images of (a) the ZnO nanowalls grown on the patterned buffer layer, (b) the ZnO nanowires on the non-patterned ZnO buffer layer, and (c) the ZnO nanowires on the sapphire substrate

The patterned buffer layer was put on the SiC plate heated at 750 °C in the vacuum chamber filled with Ar gas at a pressure of 26.7 kPa, and ZnO nanostructures were synthesized on the buffer layer by ablating a pure ZnO sintered target for 60 minutes. Fig. 3 (a) shows the SEM image of ZnO nanowalls synthesized on the patterned buffer layer. Vertically-aligned ZnO nanowalls were grown at edge of the patterned lines. The maximum height of ZnO nanowall was about 4.5 μm, and the average thickness of the ZnO nanowall was about 200 nm. On the other hand, vertically-aligned nanowires were grown at the non-patterned buffer layer, as shown Fig. 3 (b). The nanowires have a diameter of 100-150 nm. In Fig. 3 (a), similar nanowires can be seen between the nanowalls, on which no laser beam was irradiated. In contrast, random nanowires were grown on the sapphire substrate, as shown in Fig. 3 (c). The results show that the buffer layer works to align the nanowires, and patterned buffer layer enhances the nucleation and growth rate of the nanowires [15].

III. Optical Characteristic of ZnO Nanowalls

A. Lasing in Single Piece of ZnO Nanowall

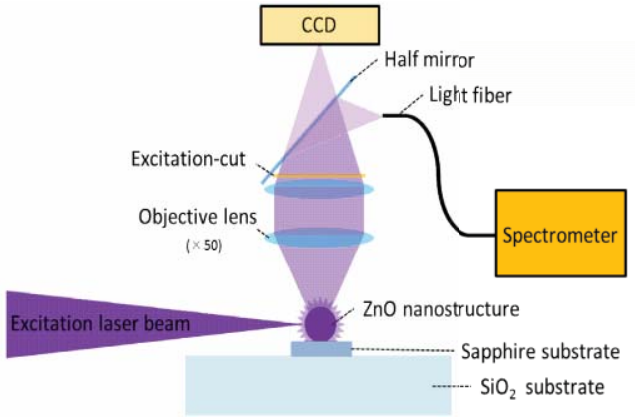

Fig. 4 Schematic of the microscopic-spectroscopy system

The optical characteristic of the ZnO nanowalls was investigated by microscopic-spectroscopy system. Fig. 4 shows the experimental arrangement image. Excitation light was the third harmonic of a Q-switched Nd:YAG laser (355 nm, t = 5 nm), and the excited nanostructures were observed by a CCD camera. The emission from the ZnO nanowalls were observed by a spectrometer having measuring area of about 10 μm in diameter through an optical fiber.

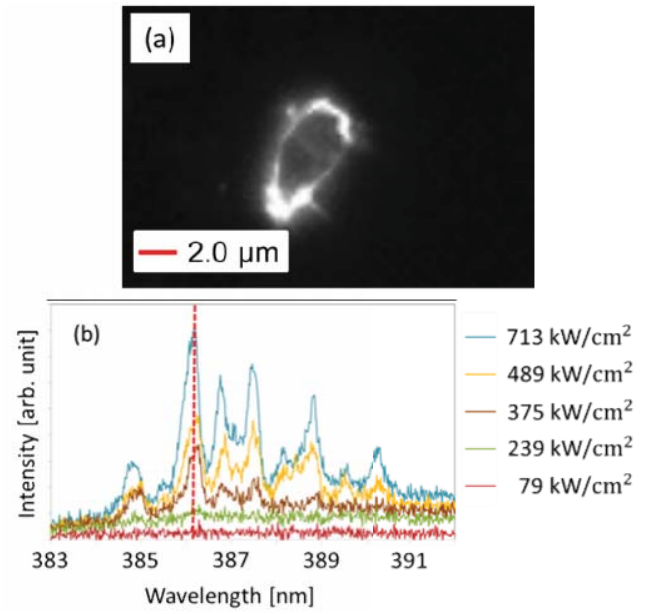

Fig. 5 (a) CCD image of single piece of ZnO nanowall under excitation, and (b) PL spectra of a piece of ZnO nanowall for different excitation power densities

At first, lasing in single piece of the ZnO nanowall was investigated. The pieces of the ZnO nanowalls were removed from the synthesized sample, and they were dispersed on another sapphire substrate. Fig. 5 (a) shows the CCD image of single piece of the ZnO nanowall under excitation. The nanowall has the long side length of about 6.3 μm and the thickness of 200 nm. Fig. 5 (b) shows the photoluminescence (PL) spectra of the ZnO nanowall for different excitation power densities. When the excitation power density was increased, the modal structure became observable. Fig. 6 shows the normalized peak intensities plotted as a function of the excitation power densities at 386.2 nm. The estimated threshold power density for lasing was about 150 kW/cm^2. It is considerably lower than the lasing threshold of ZnO nanowire which is about 200 ~ 400 kW/cm^2 [5]. It indicates that a ZnO nanowall can be a superior laser medium compared to a ZnO nanowire. On the other hand, there is no regularity in the mode spacing shown in Fig. 5 (b). It is considered that emission light

propagates inside the nanowall by the reflection at the boundary of ZnO and air, and then random oscillation routes inside the nanowall would be formed due to the distorted shape.

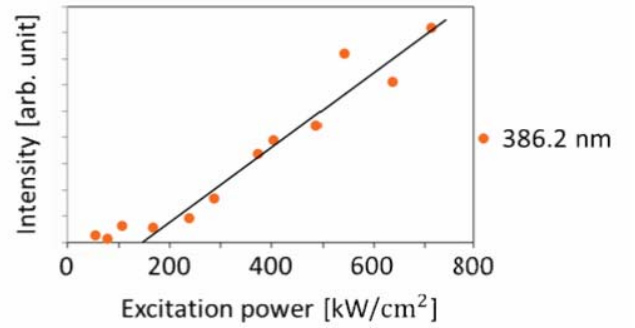

Fig. 6 The peak intensities plotted as a function of the excitation power densities at 386.2 nm

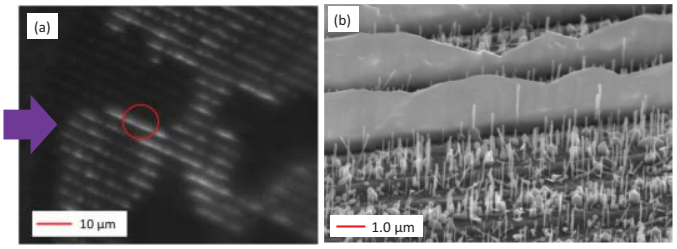

Fig. 7 (a) CCD image of the vertically-aligned ZnO nanowall array under excitation, and (b) the SEM image of the ZnO nanowalls shown by the circle in Fig. 7 (a)

B. Lasing from Vertically-Aligned ZnO Nanowall

Next, the vertically-aligned ZnO nanowalls were directly excited. However, no lasing from other many nanowalls was obtained. It may be due to the leakage of the emission light generated inside the nanowall into the buffer layer. In contrast, lasing from a few numbers of the nanowalls was achieved because of relative low leakage of the light. Fig. 7 (a) shows the CCD image of the excited ZnO nanowalls captured by the CCD camera, and lasing from the nanowall shown by the circle in Fig. 7 (a) was obtained. Fig. 7 (b) shows the SEM image of the ZnO nanowalls. Fig. 8 shows the PL spectra of the ZnO nanowall for different excitation power densities. Excitation light was irradiated from the side of the ZnO nanowall. The direction of the irradiation beam was shown by arrow in Fig. 7 (a). As the excitation power density increased, the UV emission increased, and sharp modal peaks around 387.5 nm were appeared, which indicate the start of the lasing. Fig. 9 shows the peak intensities plotted as a function of the excitation power densities at 387.6 nm. The estimated threshold excitation power density for lasing was about 1150 kW/cm^2 which is much higher than that of single piece of ZnO nanowall because of the leakage of the light into buffer layer. However, lasing from the vertically-aligned ZnO nanowall was achieved for the first time. Moreover, other ZnO nanowalls were excited from three different angles by rotating in-plane, as shown in Figs. 10 (a)-(c). Changing the irradiation angle may induce not only the excitation power density but also the escitation area because of shadowing by surrounding nanowalls. PL spectra of the ZnO nanowall shown by circle in Fig. 10, which shows the same part of the same nanowall, were measured under excitation at different irradiation angles. Fig. 11 shows the spectra from the nanowall at different angles. The number of modal peaks and their peak wavelengths were changed with different irradiation angles, indicating the different oscillation routes are formed inside the vertically-aligned ZnO nanowall. The results conclude that the ZnO nanowall can work as random laser medium and the vertically-aligned ZnO nanowall array is expected to be applied to random lasing devices.

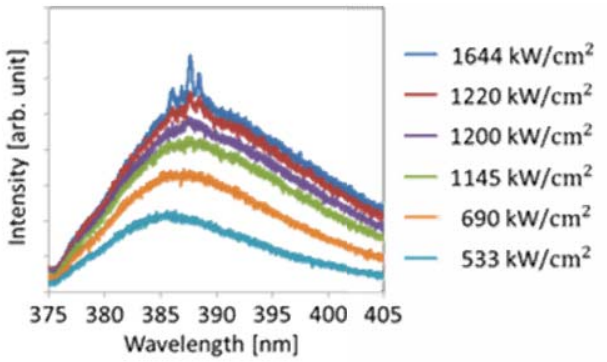

Fig. 8 PL spectra of the vertically-aligned ZnO nanowall

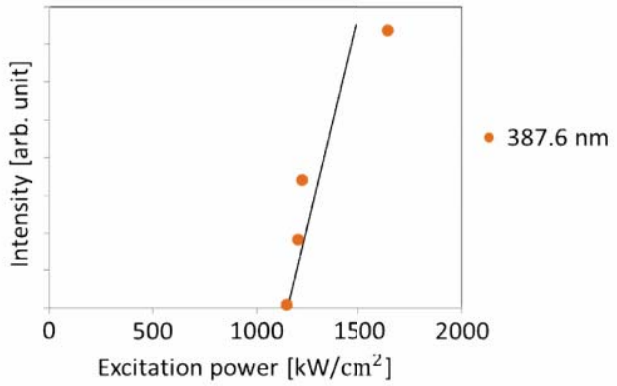

Fig. 9 The peak intensities plotted as a function of the excitation power densities at 387.6 nm

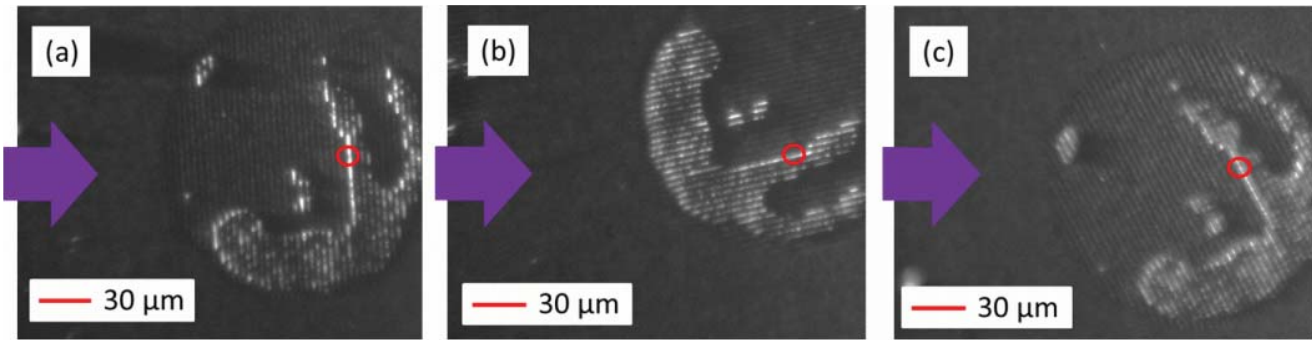

Fig. 10 The CCD images of the vertically-aligned ZnO nanowall array excited from different angles of (a) 92°, (b) 20°, and (c) 120°

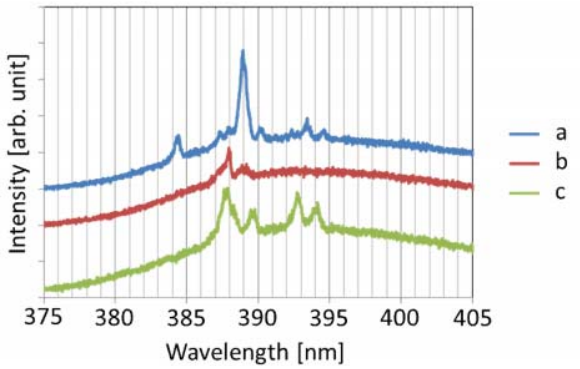

Fig. 11 PL spectra of the vertically-aligned ZnO nanowall excited from different angles as shown in Fig. 10.

IV. Conclusion

Vertically-aligned ZnO nanowalls were synthesized by NAPLD method on ZnO buffer layer patterned by two-beam interference patterning. The size of the ZnO nanowall was that the maximum height was about 4.5 μm, and the average thickness was about 200 nm. Random lasing from a piece of ZnO nanowall was obtained due to high-light confinement. In addition, lasing from the vertically-aligned ZnO nanowall having relative low leakage of the light was achieved for the first time, and the threshold excitation power density was estimated about 1150 kW/cm^2. Moreover, PL spectra from the ZnO nanowalls were changed by changing irradiation angle. Our results demonstrate the potential application of the vertically-aligned ZnO nanowall array for random lasing devices.

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