

## Two-photon absorption induced photoluminescence in a ZnO nanostructure

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### ABSTRACT

We report on experimental results of non-resonant two-photon absorption-induced photoluminescence in ZnO nanostructures, which may act as a possible route to excite ZnO nanostructure based lasers. Epitaxial ZnO nanorod-like nanostructure was grown on pre-seeded Si (100) substrates by chemical vapor deposition (CVD) method with a mixed ZnO/C solid source. Crystalline ZnO seeds were prepared and controlled by the rapid thermal annealing (RTA) treatment of e-beam deposited amorphous ZnO thin films with various thicknesses.

### INTRODUCTION

ZnO is very interesting and promising optical material because it has a room temperature direct band gap of 3.37 eV [1] and excitonic binding energy of 60 meV [2]. However, it remains very challenging to make it as a truly useful optoelectronic material. One of the challenges is to epitaxially grow ZnO on a suitable substrate although thin film deposition on various substrates such as silicon or sapphire wafers using different methods has been successful [3]. Another challenge is to understand and control the high level of non-intentionally doped residual electron density. This not-yet controllable residual electron density [4, 5] is the reason behind the inability of making ZnO a good p-type material necessary optoelectronic devices. It also limits the full potential of large exciton binding energy because of carrier screening effect.

Despite this drawback, there are increasing amount of works [6-8] on further exploring its optical properties of this material with hope that the material issue will be soon solved in joining the success of GaN-related materials. Most of reports, however, are based on single-photon excitation such as single-photon pumped ZnO UV lasers. On the other hand, the none-central -symmetry of the wurtzite structural ZnO should have good nonlinear multi-photon effects which have potential application in multi-photon absorption fluorescence microscopy, three dimensional optical data storage, frequency up-conversion luminescence and lasing, and optical limiting owing to high spatial resolution and large penetration depth of excitation light.

In this work, we report on the experimental results of non-resonant two-photon absorption-induced photoluminescence in a ZnO nanostructures from at room temperature. The ZnO nanorod-like nanostructure was epitaxially grown on pre-seeded Si (100) substrates by Chemical Vapor Deposition (CVD) method with a mixed ZnO-powder/C-powder solid source. Crystalline ZnO seeds were prepared and controlled by the rapid thermal annealing (RTA) treatment of e-beam deposited amorphous ZnO thin films with various thicknesses.

## EXPERIMENTAL RESULTS AND DISCUSSION

Amorphous films with thickness from 200 to 600 nm were deposited on Si (100) substrates by e-beam evaporator and then rapid thermal annealed under N<sub>2</sub> with various annealing temperature and time period. These films were then studied by scanning electron microscopy and photoluminescence. Fig. 1a and 1b display the seed film used to epitaxially grow nanorods reported in this work. Fig. 1a is a relatively large scale image indicating clearly domain size on order of 100 μm; while Fig. 1b is 200 nm scale SEM image showing most of crystallites have a well defined orientation of (0001) direction.

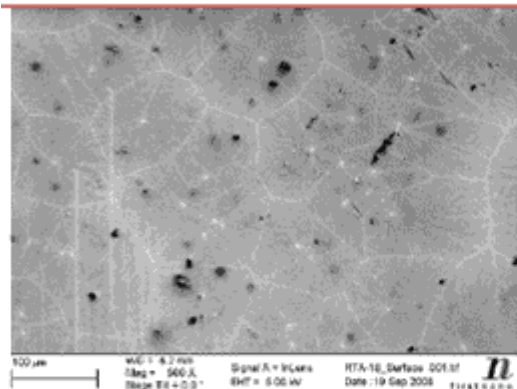


Fig. 1a SEM image of rapid thermally annealed ZnO amorphous film.

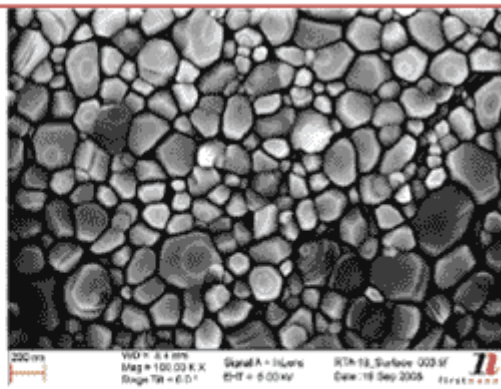


Fig. 1b Same as Fig. 1a but with large magnification.

Rapid thermal annealed films were then characterized by photoluminescence (PL). PL spectra were measured by Horiba NanoLog system coupled with an optical cryostat (4 to 350 K) from Advanced Research System as shown in Fig.2. The 9 K photoluminescence spectrum is displayed in Fig. 3 for the ZnO seeded film, RTA-18, on which nanorods were grown. From the PL intensity variation with temperature, three main PL peaks are identified as A-band free exciton, XA (3.365 eV), donor-bound exciton, XD (3.328 eV), and phonon replica of XA (3.255 eV). The so-called green is very weak indicating very low optically active defect density in these films.

A commercially built vapor deposition (CVD) system (First Nano, ET2000) was used to epitaxially grow (we call it nano-epi) nanostructures on these pre-seeded substrates. This system was equipped with a separated solid source heater, a three-zone (load, center, and end zone) furnace, a gas injector, a vacuum pump, and a quartz tube. The reaction tube was controlled by a three-zone furnace to obtain a uniform temperature across the substrate at the collecting area over 3 inches by 2 inches. The source material was mixed ZnO powder (Alfa Aesar, 99.99%) and graphite powder (Alfa Aesar, 99.995%) with mass ratio of 1:4. The solid source was placed at the load zone in the quartz tube and heated up to high temperature by an additional solid source heater to generate Zn vapor which was then carried into the center zone by the Ar carrying gas. The reacting gas (O<sub>2</sub>) was introduced into the system by gas injector.

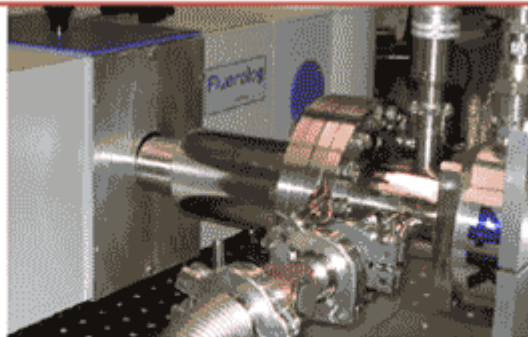


Fig. 2 Photoluminescence apparatus used in this work.

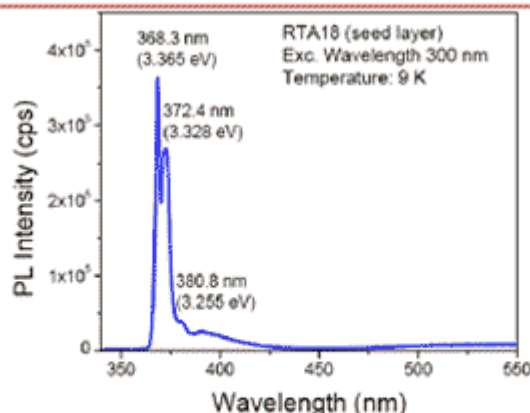


Fig. 3 Photoluminescence spectrum from the ZnO seeded film at 9 K.

Fig. 4a (with a 1  $\mu\text{m}$  scale) and 4b (200 nm scale) display the SEM images of irregular nanorods epitaxially grow on the ZnO seeds. Room temperature PL spectrum was taken from these epitaxially grown nanorods. Its peak intensity is at least 3 times stronger than that from bare seed film as shown in Fig. 5a. The normalized 9 K PL spectrum from ZnO nanorods is also displayed in Fig. 5b as compared with that from the bare ZnO seed layer. It appears that the PL originated from donor-bound exciton is either much weaker or completely disappeared suggesting these ZnO nanorods epitaxially grown on the ZnO seeds might be residual-donor-free material.

Two-photon absorption induced PL was excited by 532 nm laser line for an Nd: YVO laser (8 ps pulse width, 76 MHz repetition rate). A log intensity plot of excitation dependence of PL spectra taken at room temperature is displayed in Fig. 6a. It should be noticed that PL peak,  $\sim 378$  nm, is at the same position as the PL spectra excited by one photon excitation. This behavior is distinctly different than the two-photon absorption induced PL from thick films, in which PL peak is red-shifted due to self absorption. A linear plot of the two-photon induced PL spectrum at the excitation power of 488 mW is shown in Fig. 6b with negligible green emission at 550 nm, consistent to our suggestion of the high optical quality of these nanorods.

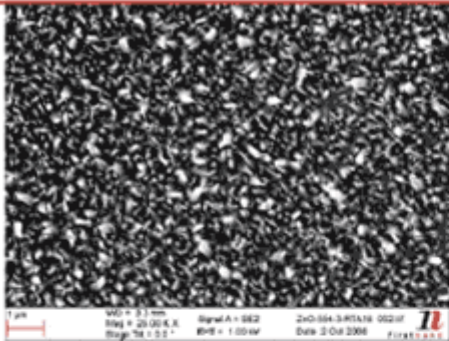


Fig. 4a SEM image of ZnO nanorods epitaxially grown on ZnO seeded layer.

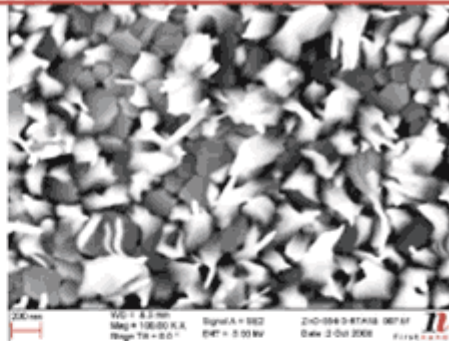


Fig. 4b Same as Fig. 4a except with high magnification.

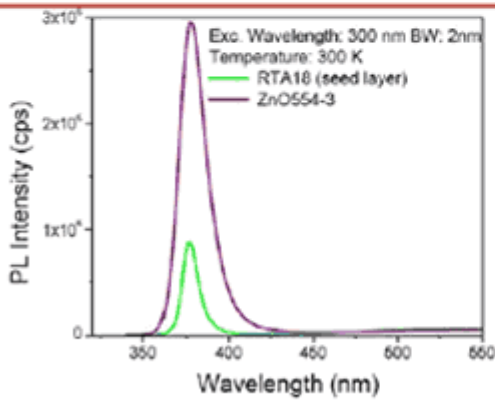


Fig. 5a Room temperature PL spectrum of ZnO nanorods as compared to that from the bare seed layer (green curve).

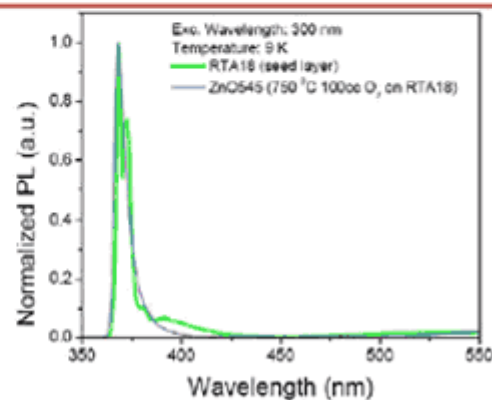


Fig. 5b Normalized 9 K PL spectrum of ZnO nanorods as compared to that from the bare seed layer (green curve).

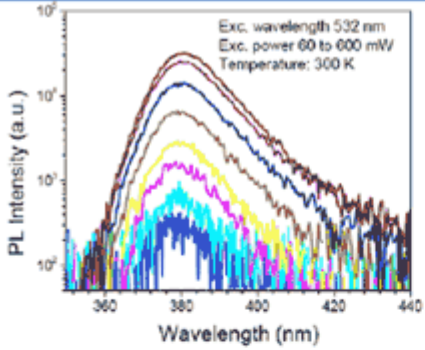


Fig. 6a Two photon absorption induced PL spectra at different excitation power.

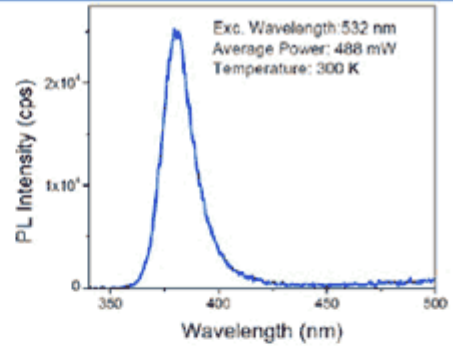


Fig. 6b Two-photon induced PL spectrum at the excitation power of 488 mW.

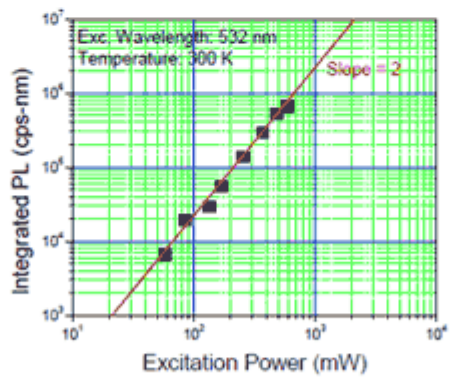


Fig. 7 Integrated 2-photon absorption induced PL intensity as a function of excitation power at room temperature.

Finally, the integrated PL intensity excited by 532 nm laser is plotted as a function excitation power in Fig. 7. It clearly shows that its variation with the excitation power has an exact slope of 2 indicating unambiguously two-photon absorption process is the excitation mechanism for the measured PL excited below their band gap in these ZnO nanorods.

**CONCLUSIONS**

Our preliminary experimental data on two-photon absorption induced photoluminescence are reported from ZnO nanorods epitaxially grown on a ZnO pre-seeded film. This system might provide a platform to study nonlinear optical processes in various ZnO nanostructures.

**ACKNOWLEDGMENTS**

The authors would like to acknowledge the partial financial support from NYSTRA grant for this work through the CUNY center of advanced technology on photonic applications.



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