

ZnO nanostructures epitaxially grown on ZnO seeded Si (100) substrates by Chemical Vapor Deposition

Zhuo Chen¹, T. Salagaj², C. Jensen², K. Strobl², Mim Nakarmi¹, and Kai Shum^{1, a}

¹Physics Department, Brooklyn College of the City University of New York, 2900 Bedford Avenue, Brooklyn, NY 11210, USA

²First Nano, a division of CVD Equipment Corporation, 1860 Smithtown Avenue, Ronkonkoma, NY 11779, USA

ABSTRACT

ZnO nanostructures such as nanowire-networks and vertical nanorods were epitaxially grown on pre-seeded Si (100) substrates by chemical vapor deposition (CVD) method with a solid source. Crystalline ZnO seeds were prepared and controlled by the rapid thermal annealing (RTA) treatment of e-beam deposited amorphous ZnO thin films. Both epitaxially grown ZnO nanostructures and pre-deposited ZnO seeds were characterized by scanning electron microscopy (SEM), and photoluminescence (PL) spectroscopy. Excellent optical characteristics of these nanostructures such as PL line width, linearity of PL intensity as a function of excitation power density were obtained.

INTRODUCTION

SEMiconductor industry continuously brings new inventions into our daily life. For example, the mass-producible and high-quality blue-ultraviolet GaN-based light emitting diodes and lasers are used in blue-ray DVDs, displays, and traffic signals. ZnO is an II–VI SEMiconductor with a wurtzite structure. It has a wide direct band gap of 3.37 eV [1] at room temperature and a large exciton binding energy of 60 meV [2], theoretically ensuring a more efficient excitonic emission at room temperature than that from GaN counterpart even under low excitation intensity.

In attempts to grow high quality ZnO films on suitable substrates using various methods such as metal-organic vapor-phase epitaxy (MOVPE), various ZnO nanostructures, instead, have been successfully grown and characterized. [3-5] In this paper, preliminary experimental data are reported on epitaxial growth ZnO nanostructures on pre-seeded ZnO films by chemical vapor deposition method using a solid source. These ZnO nanostructures are then characterized by scanning electron microscopy and photoluminescence.

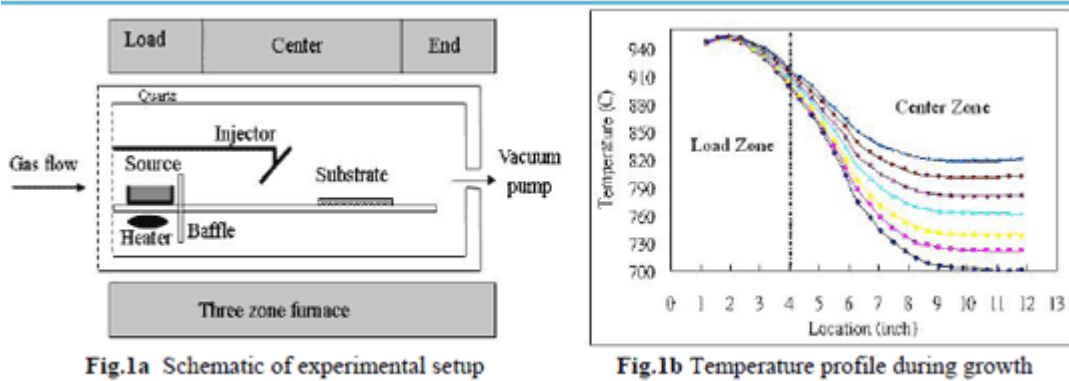
EXPERIMENTAL DETAILS

Because of the large lattice mismatching between crystal ZnO and Si (100), it is difficult to deposit high quality ZnO nanostructure directly on Si (100). A three-step method was investigated in this work. First step, amorphous ZnO films with thickness from 100 to 600 nm was deposited on Si by e-beam evaporator. For the second step, these films were rapidly thermal annealed at 900 °C in Ar gas for 30 minutes. In the last step, a CVD system (First Nano, ET 2000) was used for epitaxial growth. This system was equipped with, a solid source heater, a three-zone (load, center, and end zone) furnace, a quartz paddle/plate/baffle, a gas injector, a vacuum pump and a water cooling system. The ZnO solid source was heated up to 950 °C by a solid source heater. The temperature of reaction zone was controlled by a three-zone furnace to obtain a uniform temperature across the substrate. The source material was a mixed ZnO (Alfa Aesar, 99.99%) and graphite powder (Alfa Aesar, 99.995%) with mass ratio of 1:4. It was placed at the load zone and heated to generate Zn vapor. The carrying gas of Ar was used to transport the Zn vapor to reaction zone. The reacting gas of O₂ was introduced into the system by gas injector. Fig. 1a shows the

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schematic diagram for the CVD apparatus. Fig 1b displays typically measured temperature profiles across load to center zone.



Photoluminescence (PL) spectra were measured by Horiba NanoLog system coupled with an optical cryostat (4 to 350 K) from Advanced Research System.

RESULTS AND DISCUSSIONS

In Fig. 2a, 2b, and 2c, SEM images were displayed for the amorphous ZnO, RTA-ZnO, and epitaxial nanorods films produced in our three-step method. For the amorphous film, the granular particles have a size of 20 to 50 nm. After a thermal annealing treatment, ZnO crystallites appear with a well defined orientation. The crystallites will serve as seeds on which nanorods will be epitaxially grown on as shown in Fig. 2c.

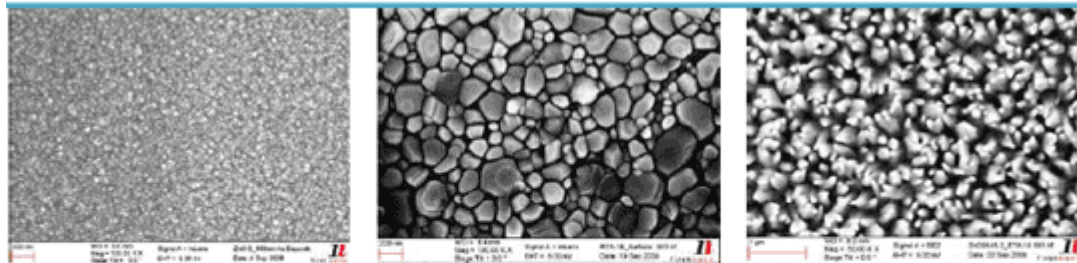


Fig.2a SEM of Amorphous ZnO surface on Si (100)

Fig.2b SEM of ZnO surface after RTA.

Fig.2c SEM of Epitaxial ZnO nanorods surface.

Fig. 3 displays a cross section SEM for the nanorod structure grown epitaxially (nano-epi). Carefully exam this SEM, it is not difficult to find that there are two layers of nanostructures. The first layer is directly grown on the seeds with different sizes acting as a buffer layer. The second layer consists of well defined more uniform nanorods with height of 200 to 300 nm.

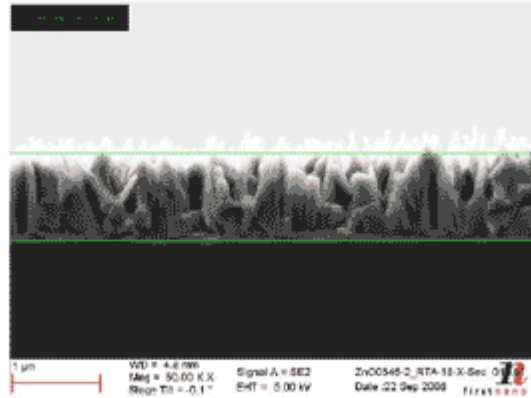


Fig. 3 The cross section SEM image of nanorod layer.

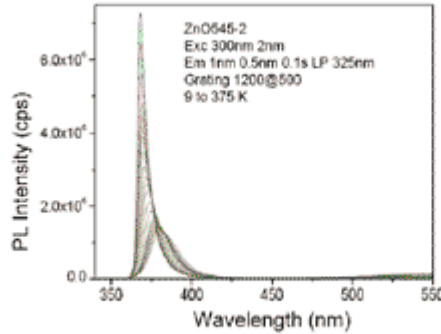


Fig. 4 Temperature dependence of PL spectra of ZnO nanorods.

Fig. 4 shows the temperature dependence of PL spectra taken from the ZnO nanorods epitaxially grown on a pre-seeded Si (100) substrate. It clearly demonstrates high crystalline quality of the nano-epi grown ZnO nanorods from the disappearance of strong donor-related exciton emission peaks and the weak green emission around 500 nm.

Fig. 5b displays the excitation power dependence of PL spectra obtained from another ZnO nanowire system obtained by our three-step method with its best individual nanowire (needle) SEM image shown in Fig. 5a. PL peak intensity is plotted as a function of excitation power in Fig. 6. It clearly shows the expected linearity (over the four order of magnitude of excitation power) for exciton emission in these high quality ZnO nanowires.



Fig. 5a SEM image of a single ZnO nanowire (needle) of ~ 1.4 μm long and 100 nm radius at the bottom.

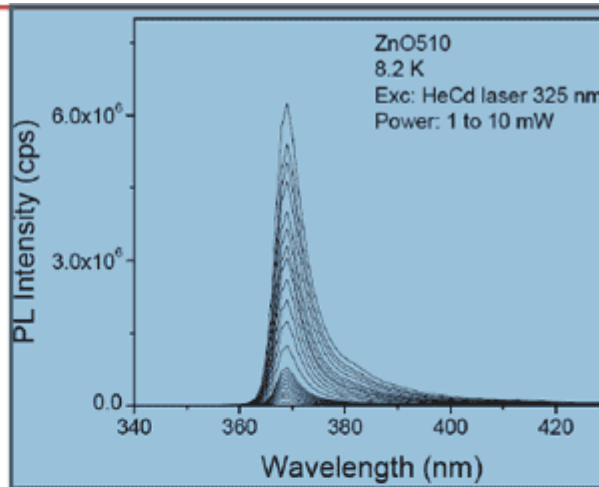


Fig. 5b Excitation power dependence of PL spectra from ZnO nanowire network (the individual nanowires are similar what is shown on the left) at 8.2 K.

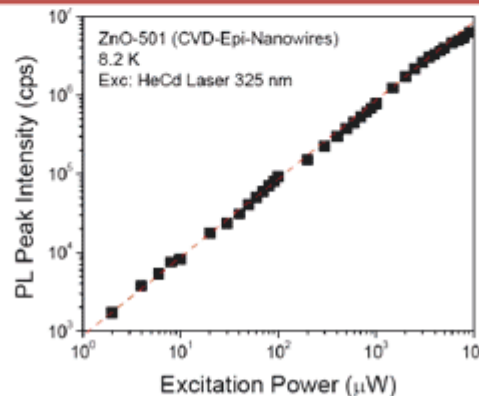


Fig. 6 The PL peak intensity as a function of excitation power at 8.2 K for the high optical quality of ZnO nanowire network.

CONCLUSIONS

Vertically ZnO nanorods/nanowires were grown using our three-step method. SEM images revealed that the resulting ZnO nanorods/nanowires were single crystals that had grown along the c axis. Furthermore, we confirmed their excellent optical emission characteristics expected exciton-related process.

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