ZnO thin film deposition on sapphire substrates by chemical vapor deposition

Zhuo Chen[1], T. Salagaj[2], C. Jensen[2], K. Strobl[2], Mim Nakarmi[1], and Kai Shum[1, a]

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

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

[a]kshum@brooklyn.cuny.edu

ABSTRACT

ZnO thin films with thickness around 200 nm were deposited on a-plane sapphire substrates by Chemical Vapor Deposition (CVD) method with a mixed ZnO-powder/C-powder solid source. These films were characterized by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and photoluminescence (PL) spectroscopy. The correlation between surface structural properties of ZnO thin films and their optical signature measured by temperature dependence of PL is investigated for various growth conditions such as flow rate O_2 injection gas and growth temperature. At room temperature, the columbic interaction enhanced absorption edge of 3.305 eV of these films was determined by optical absorption measurements.

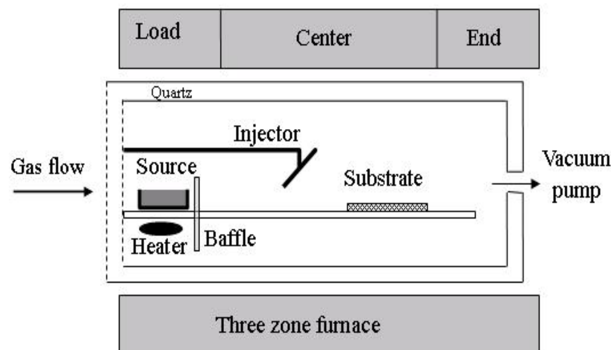
INTRODUCTION

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.

In this work, we report on the experimental data resulting from our attempt to understand how ZnO can be grown on a sapphire substrate by a solid-vapor-solid process in a commercially built chemical vapor deposition (CVD) apparatus using a solid source. Various growth parameters such as growth temperature and O_2 gas injection rate were used to alter the ZnO nucleation process. Deposited films were characterized by scanning electron microscopy and photoluminescence. We found that ZnO films could be grown by the CVD method with the film quality comparable to these grown by more expensive apparatuses such as metal-organic chemical vapor deposition (MOCVD).

EXPERIMENTAL DETAILS

A commercially built vapor deposition (CVD) system (First Nano, ET2000) was used to deposit thin film on sapphire substrates. It 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%) 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_2) was introduced into the system by gas injector at different locations to achieve the best uniformity over a given substrate size. Sapphire substrates with a-plane cut were used. Fig. 1a shows the schematic diagram for the CVD apparatus. Fig 1b displays typically measured temperature profiles across load to center zone. Two important parameters, growth (substrate) temperature (T_g) and O_2 flow rate (F_{O2}) will be discussed in this work. The surface morphology of deposited thin films was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Optical transmission/absorption spectra were measured from PerkinElmer Lambda950 optical spectrometer. Photoluminescence (PL) spectra were measured by Horiba NanoLog system coupled with an optical cryostat (4 to 350 K) from Advanced Research System.



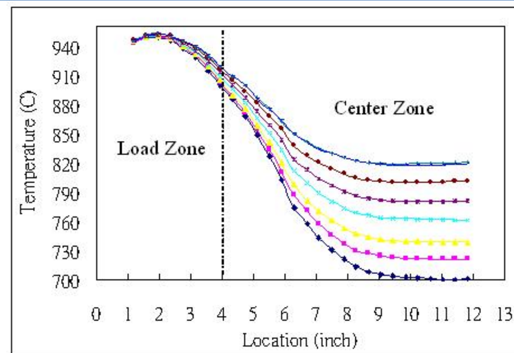
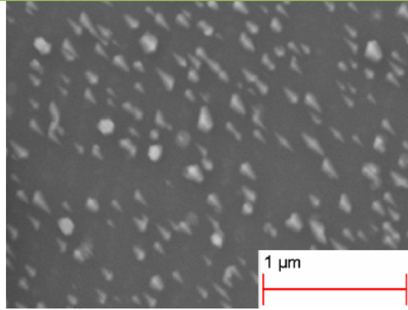
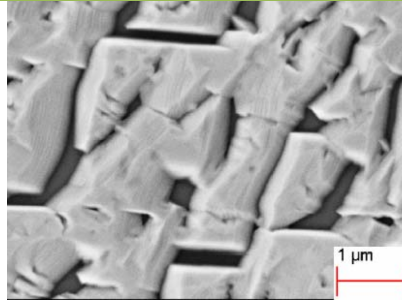


Fig. 1a Fig.1b

RESULTS AND DISCUSIONS

Fig. 2a, 2b, and 2c display the SEM surface images for the 3 samples placed in the center zone with different growth temperature of 720, 820, and 920 ^oC, respectively, for 1 hour deposition time. It is clear that at 720 ^oC ZnO starts to nucleate on the sapphire surface, but the speed the film growth is too slow, leading to the scattered ZnO islands on the sapphire surface during 1 hour time period. At 820 ^oC, the speed of nucleation has dramatically increased and left a thin layer of ~ 200 nm during 1 hour. Since the ZnO coverage on the sapphire surface is not 100%, therefore, the thickness of ZnO thin film was measured by AFM as shown in Fig. 3. At 920 ^oC, no visible ZnO film was deposited on the substrate.





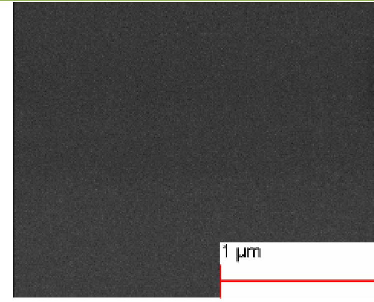


Fig. 2a ZnO on sapphire substrate at 720 °C.

Fig. 2a ZnO on sapphire substrate at 820 °C.

Fig. 2a ZnO on sapphire substrate at 920 °C.

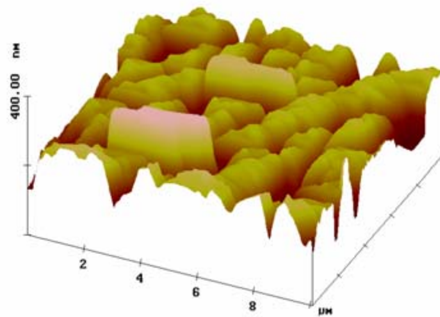
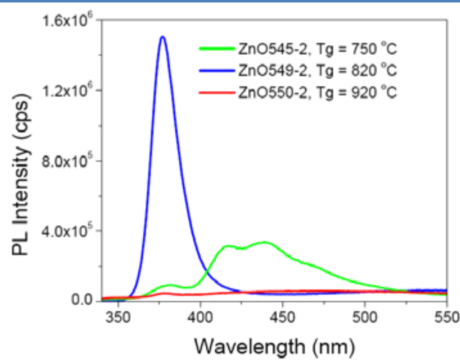


Fig. 3 AFM image of the 820 °C sample.



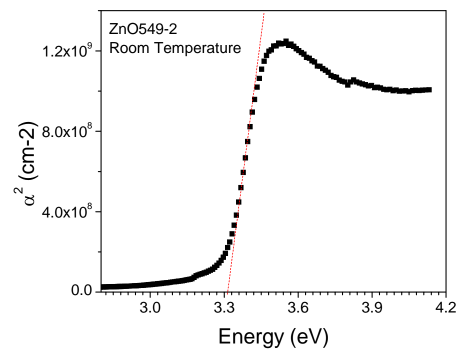


Fig.4a PL spectra from 3 samples with different growth temperature.

Fig. 4b Tauc plot to obtain the optical band gap for the 820 °C sample.

Photoluminescence was measured from these 3 samples at room temperature with a Xe-lamp set at 300 nm with band pass of 5 nm as a photoexcitation source. They are shown in Fig. 4a as green, blue, and red curves for the sample with the growth temperature of 720, 820, and 920 ^{o}C, respectively. All three spectra show a band edge emission at ~378 nm with negligible green emission at 550 nm, normally attributed to defect-related emission. PL from the film with growth temperature of 820 ^{o}C is certainly strongest among the three samples, consistent with the information provided by their SEM images. The origin of three weak PL peaks from 400 to 500 nm for the 720 ^{o}C sample is not clear.

In Fig. 4b, a Tauc plot [6] is displayed for the 820 ^{o}C sample. The optical band gap of 3.31 eV is obtained. This energy is consistent with other ZnO thin films obtained by other methods [7, 8] and with generally accepted ZnO band gap [1] at room temperature by taking into the excitonic effect on absorption edge.

With apparently optimal growth temperature of 820 ^{o}C on sapphire substrate, three ZnO films were deposited with different O_2 flow rate at 100, 500, and 1,000 standard cubic center meter per minute (with a short notation of cc). The SEM images for these three samples are shown in Fig. 5a, 5b, and 5c, respectively. For the 100 cc sample, it is clearly visible that there is a large amount of surface defects (pits). However, the estimated number of pit density seems to be on the order of 10^7 cm^{-2}, comparable with these thin films deposited [9] by more expensive apparatus MOCVD. Such defect density decreases as the O_2 flow rate increases as shown in the 500 cc and 1000 cc samples.

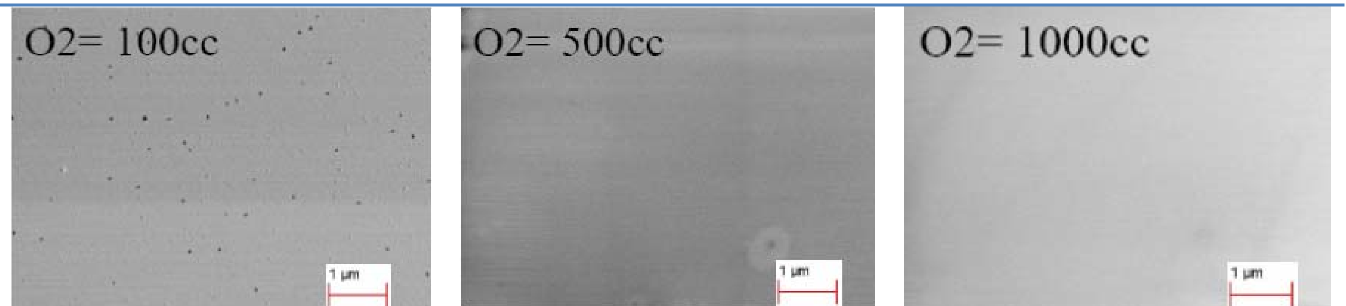


Fig. 5a ZnO film on sapphire substrate with O2 flow rate of 100 cc.	Fig. 5b ZnO film on sapphire substrate with O2 flow rate of 500 cc.	Fig. 5c ZnO film on sapphire substrate with O2 flow rate of 1,000 cc.

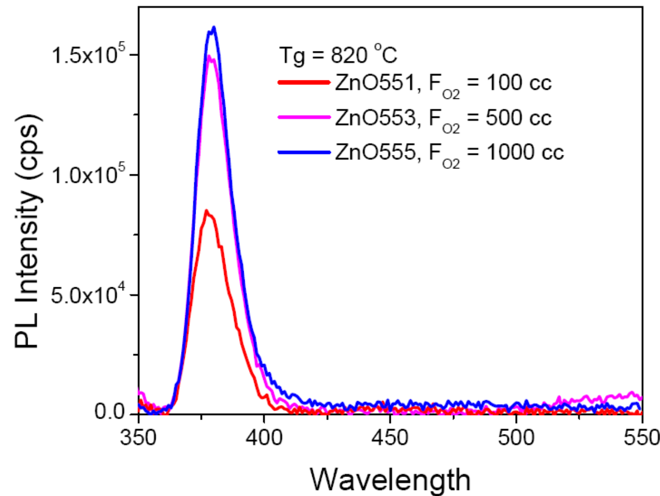


Fig. 6 PL spectra from the three samples with the different O_2 flow rate as indicated in the figure.

PL spectra for the three samples with different O_2 flow rates are displayed in Fig. 6. The PL peak intensity seems to be consistent with the pit density as obtained from SEM images. Although the data points are limited, apparently, the PL intensity (I_{PL}) has a square root relationship with the O_2 flow rate, i.e., $I_{PL} \sim F_{O2}^{1/2}$.

CONCLUSIONS

In summary, we have presented our preliminary data on ZnO thin film deposition by CVD method using a solid source. It was found that the optimal growth temperature is 820 ^{o}C and the film surface pit density decreases while photoluminescence intensity increases as the O_2 flow rate increases. These films clearly show good poly-crystalline quality with low optically active defect density as evidenced by the lack of so-called green emission around 550 nm.

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