## FABRICATION AND I-V CHARACTERIZATION OF ZnO NANOROD

# BASED METAL-INSULATOR-SEMICONDUCTOR JUNCTION

Le Hong QUANG<sup>2</sup>, CHUA Soo Jin<sup>2</sup>, Eugene A. FITZGERALD<sup>1</sup>

<sup>1</sup> Massachusetts Institute of Technology <sup>2</sup> National University of Singapore

Abstract —We report on the characteristics of a ZnO based metal insulator semiconductor (MIS) diode comprised of a heterostructure of n-ZnO nanorods/n-GaN. The MIS structure consisted of unintentional - doped n type ZnO nanorods grown on n-GaN sample using hydrothermal synthesis at low temperature (100<sup>0</sup>C). The ZnO nanorod layer was vertically grown from the GaN sample, having the diameter 100nm and length 2µm. Then, an insulator layer for electrical isolation was deposited on the top of ZnO nanorod layer by using spin coating method. A metal layer (gold) was finally deposited on the top. The I-V dependences show a rectifying diode like behavior with a leakage current of 2.10<sup>-5</sup> A and a threshold voltage of about 4V. Depend on the thickness of the insulator, the I-V dependences of the n-ZnO/n-GaN heterostructure was varied from rectifying behavior to Ohmic and nearly linear.

*Index Terms* — Gallium Nitride, Metal Insulator Semiconductor structure, Nanostructure, Zinc compounds

#### I. INTRODUCTION

 $\mathbb{Z}_{popular}$  material due to its great potential for optoelectronic applications. The large direct band gap (3.3437 at 2K), along with large exciton binding energy (60meV), amenability to conventional chemical wet etching and availability of large area substrates at relatively low cost, make ZnO a strong candidate for the next generation of ultraviolet light emitting and lasing devices operating at high temperatures and in hash environments [1] In the last few decades, one dimensional semiconductor nanostructures, such as nanorods and nanowires, have become important fundamental building block for nanophotonic devices and offer substantial promise for integrated nanosystems. In nanostructure, the density of states of carrier is concentrated at some specific energy levels, which enable enhancement of exciton oscillator strength and light emitting efficiency. As a result, the performance of nanostructure based optical devices is

Author Chua Soo Jin Email: elecsj@nus.edu.sg

expected to improve and to be less temperature dependence.

Recently, much attention has been paid to the nanostructure ZnO materials which radiate ultraviolet UV emission. It is expected that a lower threshold optical pumping density for lasing is due to the carrier confinement effect in 1D nanostructure. Moreover, the binding energy of exciton and biexcitons has been shown to be enhanced significantly in 2D structure such as ZnO/ZnMgO quantum wells [2]. Therefore, a stronger excitonic effect is expected in one dimensional ZnO nanostructure. All these indicate the possibility of ZnO nanostructure's application in exciton based photonic devices.

In this report, the ZnO nanorods were epitaxially grown by using aqueous solution. This growth method showed some advantages compared with others (MOCVD, pulse laser deposition, radio frequency magnetron sputtering), such as use of simple equipment, low temperature deposition (100C), low cost, less hazardous and no need for use of metal catalysts. Here, the GaN films was used as a template for the ZnO nanorods growth since these materials have the same wurtzite crystal structure, low lattice constant misfit (1.9%) and similar thermal expansion [3]. Due to similar crystal properties, the ZnO nanorods are expected to epitaxially grow on the GaN template.

As been known, the fabrication of light emitting ZnO based homojunction emitters still remain problematic because a high quality and reproducible p-type ZnO is difficult for manufacturing, despite much progress made in this direction [4,5]. Fortunately, many of the advantages of ZnO can also be realized by the fabrication of the ZnO based heterojunctions and metal-insulator-semiconductor (MIS) diodes. So far, there are no recent reports and only two old publications [6,7] In [6], a MIS diode was fabricated with an insulating ZnO layer obtained by keeping the ZnO crystalline a 30% solution of  $H_2O_2$ . In [7], an insulating SiO layer was used.

In this work, the polystyrene was employed to

produce an insulating layer on ZnO nanorods by spin coating method. The experimental techniques was explained in the following part.

### II. EXPERIMENTAL TECHNIQUES

A schematic of n-ZnO nanorod based metal-insulator –semiconductor junction is shown in figure 1.

The EMCORE D125 MOCVD system was used to grow 3µm GaN on c plane sapphire at 1020C. This GaN film would be used as a template to grow ZnO nanorods. The experiment procedure for ZnO nanorod growth was designed as follows: Zinc acetate Zn (CH<sub>3</sub>COO)<sub>2</sub> .2H<sub>2</sub>O was first dissolved in deionized water at room temperature. Then, NH4OH was added into the solution to create the alkaline environment (pH~10). The resulting suspension was transferred into a Teflon- lined stainless steel autoclave. Next, the GaN sample, after cleaning with deionized water, was dipped into the solution and suspended in the autoclave by a tantalum wire. Finally, the autoclave was sealed and put into the oven. The hydrothermal treatment was carried out at 100C. After the growth, the autoclave was allowed to cool down naturally. The samples were taken out, washed in the deionized water and dried in the air.

The free space between the individual ZnO nanorods was filled with a thin polymer by spin coating. The thickness of this polymer layer is controlled by the spin speed, and spin time. This was followed by the metallization of the n-ZnO nanorods; 50nm Au layer was deposited on the polymer/nZnO by electron beam evaporation, resulting a continuous contact layer. Then, one part of the sample was etched away to expose the bare n-GaN. For the metallization of n-GaN, In was deposited to obtain a good Ohmic contact. The I-V characteristics of the devices were measured by using 4 probe station systems.

#### III. RESULTS AND DISCUSSIONS

The synthesis of ZnO nanorods resulted in a preferential growth direction along the c-axis of ZnO normal to the substrate surface. As shown in figure 2a, field emission scanning electron microscopy FESEM clearly revealed the general morphology of the ZnO nanorod arrays on n-GaN, showing uniform distributions in their diameters and lengths. The average length and diameters of the nanorods grown for 3 hours are 2  $\mu$ m and 100 nm, respectively. The number density of nanorods was as high as 10<sup>9</sup> per cm<sup>2</sup>.

Figure 3 show the XRD and photoluminescence results of the ZnO nanorods. In Figure 3a, a strong peak at  $2\theta$ =34.4 due to ZnO (002) crystal plane was observed. This strong (002) diffraction peak demonstrated the oriented arrays of ZnO nanorods with a preferential growth in the caxis direction. This peak could be indexed to the hexagonal phase of ZnO. In the PL spectrum of ZnO nanorods (figure 3b), a strong peak at 385 nm was attributed to the exciton related recombination [8]. Besides, a weak green band in the range of 470-600 nm was also observed. This green band was attributed to single ionized oxygen vacancies in ZnO and the emission results from the radiative recombination of a photogenerated hole with an electron occupying the oxygen vacancy [9,10]. More detail information about the characterizations and growth of ZnO nanorods on GaN had been reported elsewhere [11]

It has been known that metallic composition of the contact is a critically important parameter for making Ohmic contacts to n-GaN. The I-V characteristics for several metal contacts on n-GaN were shown in Figs 4. The In contact showed linear I-V characteristic whereas the Au and Ti\Au contacts showed nearly linear I-V characteristic . Therefore, the In was chosen to be the Ohmic contact for the n-GaN. An annealing process at high temperature in a nitrogen or oxygen environment was necessary to decrease contact resistance and to increase adhesive force. However, for the In contact, the difference in I-V characteristic of the contact before and after annealing was not so significant.

The I-V characteristics of a n-ZnO nanorod based MIS junction were shown in figure 5 and 6. Here, we proceeded to measure 2 samples: sample A with thick insulator layer (cover the tip of the nanorods) and sample B with thin insulator layer (not cover the tip of the nanorods). The SEM images of these two sample were shown in Figure b and c, respectively. Figure 5 showed the I-V characteristic of sample A. This figure showed a quite good, rectifying behavior of the MIS junction, with a threshold voltage near 4V and a reverse current of about  $10^{-6}$  A ( current density  $4.10^{-4}$  A/cm<sup>2</sup> ). These value were a bit larger than other reports from the literature [12] According to some authors [7,13], under the forward bias of the MIS junction, holes tunnel from the metal through the insulator into the n-ZnO nanorods at high field conditions and the recombination takes place. In this model, the junction behavior is entirely determined by the thickness and the properties of the insulator layer. By optimized these factors, the quality of our MIS junction can be enhanced. For this, further investigations are required.

Figure 6 show the I-V characteristic of sample B. In this sample, a thin layer of insulator was filled within the ZnO nanorods. As a result, the tip of the ZnO nanorods can still be seen from the SEM image (figure 2c) and there is a very thin layer of insulator covering the top of ZnO nanorods. In addition, the energetic barrier for the carrier in the nZnO/nGaN is very small due to the crystal similarity of ZnO and GaN [3]. Therefore, a linear characteristic was observed in this sample. This result was consistent with other report [14] in which the I-V dependence of the n-ZnO/nGaN heterostructure was Ohmic and nearly linear.

### IV. CONCLUSION

In conclusion, n-ZnO nanorods were grown on n-GaN by using hydrothermal synthesis. Electrical isolation by spin coating an insulator layer was employed to fabricated a ZnO nanorod based metal –insulator-semiconductor junction. The fabricated junction demonstrates good, rectifying, diode like behavior with a threshold voltage of 4V and low leakage current of 10<sup>-6</sup> A. However, for further investigation, the electroluminescence measurements have to be carried out to observe the UV light emission under the forward bias. By changing the insulator layer's thickness, the I-V characteristic changed from rectifying behavior (for thick insulator layer) to Ohmic, linear behavior (thin insulator layer). This Ohmic, linear behavior is similar to the reported I-V dependence of the nZnO/nGaN heterostructure.

#### V. REFERENCES

- [1] Look DC, Mater Sci Eng B 2001, 80 383.
- [2] C.H.Chia, T.Makino, K. Tamura , Appl Phys Lett, 2003, 82, 1848
- [3] Y.Chen,D.M.Bagnal,Hang-jun Koh, Ki –Tae Park, Kenji Hiraga, Z.Zhu, T.Yao, J.Appl. Phys 84, 3912 (1998)
  [4] Look DC, Claflin B, Phys Status Solidi (b) 2004 241 624 ,
- [5] Lee E C and Chang K J 2004 Phys. Rev. B 70 115210

[6] Shimizu A, Kanbara M, Hada M, Kasuga M, Jpn J Appl Phys 1978, 17, 1435

[7] Minami T, Tanigava M, Yamanishi M, Kawamura T, Jpn J Appl Phys 1974 12 1475]

[8] Y.C.Kong, D.P.Yu,B.Zhang,W.Fang, Appl. Phys. Lett, 2001, 78,407.

[9] K.Vanheusden, .L.Warren, C.H.Seager, D.R.Tallant, J.Appl. Phys. 1996 79 7983]

[10] A Zeuner, H.Alves, D.M.Hofmanm, B.K.Mayer, Appl. Phys. Lett. 2002 80 2078.

[11] H.Q.Le, S.J.Chua,K.P.Loh, E.A.Fitzgerald , Appl. Phys. Lett. 87 2005 101908

[12] Ya.I.Alivov, D.C.Look, B.M.Chukichev et al , Solid State Electronics 48 2004 2343 .

[13] Lagerstedt O, Monemar B, Gislason H, J Appl Phys 1978, 49, 2953

[14] B.M.Ataev, Ya.I.Alivov, et al, Journal of Optoelectronics and Advanced Materials





Figure 1: Schematic illustration of a metal-insulatorn-ZnO nanorods junction



Figure 2 : (a) FESEM image of ZnO nanorod arrays grown on nGaN. ZnO nanorods are well-aligned perpendicular to the GaN surface (b) The FESEM image of ZnO nanorods , filled with thick insulator layer (c) The FESEM image of ZnO nanorods filled with thin insulator layer , the tip of the nanorods was exposed.



Figure 3 : (a) XRD patterns of ZnO nanorods on GaN (solid line). The pattern is typical for wurtzite hexagonal structure like bulk ZnO with unit cell constant of a=3.248Å and c=5.206Å (b) Room temperature micro-photoluminescence (PL) spectrum obtained from as-grown ZnO nanorods (solid line). The PL spectrum of the GaN sample without ZnO growth (dot line) was also displayed for comparison



Figure 4 : The I-V characteristics for several metal contacts : Au, Ti/Au and In



Figure 5: Current voltage characteristics of the ZnO MIS junction- thick insulator layer



Figure 6 Current – voltage characteristic of the ZnO nanorods MIS junction – thin insulator layer