Characterization of white light emitting diodes based on ZnO nanostructures grown on p-Si

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(Dated: November 5, 2007)

Abstract

In this paper ZnO nanorods and nanodots (with and without a SiO2 buffer layer) were grown on p-Si, forming p-n heterojunctions. The nanorods devices showed no electroluminescence (EL) emission but a rectifying behavior with a breakdown voltage around -4V. The nanodot devices showed EL emission under forward bias conditions. The buffer layer increased both the stability and efficiency of the devices. With the buffer layer EL emission was also observed under reverse bias.

1. Introduction

Miniaturization is a key word within the microelectronic community. The march towards smaller devices has given a lot of interesting results and is now entering into the nanometer regime. Such low dimensional structures possess novel physical properties that are of interest both for a fundamental point of view and for a technological view. With the technology today, nanostructures can be reproducibly grown and used as nanodevices. Among these low dimensional structures nanorods and nanowires (both being 1-dimensional) are of interest in many different applications. Nanorods of different semiconductor materials, such as silicon (Si), gallium nitride (GaN) and zinc oxide (ZnO), have been grown. The later, ZnO, are the topic of this paper.

Zinc oxide (ZnO) is a wide band gap semiconductor exhibiting many interesting properties making it promising for optoelectronic devices and biosensors [1]. Good up to date reviews on ZnO can be found in [1, 2]. To mention some of these properties, ZnO has a direct band gap (3.37 eV at room temperature) and shows more resistance to radiation damage than Si and GaN. ZnO also have a rich family of nanostructures and nanorods, belts, wires, tubes etc have been grown. It has also been shown that defects in ZnO give rise to the green luminescence band or deep band emission (DBE), literally the emission band between 420 and 700 nm. Its origin have for long been a matter of discussion, but recently it was suggested that the DBE could consist of several PL bands having different origin placed at similar positions [2]. Indeed, Moe Borseth et al. [3] have recently assigned the V_{O}, V_{Zn} and Li related photoluminescence (PL) bands contributing to the DBE at different wavelength. Furthermore Klason et al. [4] showed that the V_{O} and V_{Zn} related PL bands have characteristic features when decreasing the measurement temperature. In addition, ZnO has the strongest exciton binding energy (about 60 meV) making the excitons thermally stable at room temperature (RT). Accordingly, ZnO has a significant advantage for ultraviolet (UV) lasing applications. However in order to reach the full potential as optoelectronic material it is required to obtain both p-type and n-type ZnO. The undeveloped p-type doping of ZnO have long hindered fabricating homojunctions of this excellent semiconductor. However, several reports demonstrating p-type ZnO have been published [5–12] and recently Wei et al. fabricated ZnO blue-violet light-emitting diodes (LED) using a p-n homojunctions [13]. Also Ryu et al. demonstrated UV photodiodes [14] and Liu et al. have also managed to fabricate a blue-yellow LED [15] using ZnO homostructures. Several other groups have also demonstrated devices made from ZnO pn homojunctions [6, 9, 16–23]. The different colors reported from these LED were: yellow-blue and UV [15, 21], violet-white [22], blue-violent [13], blue-white [9], none [6], UV and white [19], UV lasing [20] and violet-green [23].

Recently heterojunction LED based on n-ZnO/p-Si heterojunctions thin films were demonstrated [24]. Although working LED device was demonstrated, the devices were far from being ideal regarding the transport mechanisms. This is expected as the growth thin films
of ZnO directly on Si necessitate the growth of low temperature buffer layer, and hence a sharp interface heterojunction is not well-defined. This was clear from the observed tunneling process that dominates over thermoionic emission. There have also been reported several heterostructured p-n junction, in which the n-type component was ZnO and the p-type layer was some other semiconductor material. The different p-type films and substrates used were: Si [24–29], SiC [30–32], GaN [33–36], diamond [37], SrCu$_2$O$_2$ [38], ZnRh$_2$O$_4$ [39], NiO [40], GaAs [41] and sapphire [42].

In this paper we present our preliminary results of employing ZnO semiconductor in junction with p-type Si. Also previous results with a p-SiC/n-ZnO nanorod device is shown as comparison. We grow the n-ZnO nanostructures directly on p-type substrate. This has the advantage of high quality and well defined interface between the n-ZnO and p-type substrate as evident from observed results during the last years of research. Silicon represents an attractive alternative to be investigated due to its central position in the microelectronics industry. Two different kinds of nanostructures were used, nanodots and nanorods. The ZnO nanodots devices were preformed on p-Si with and without a SiO$_2$ layer between the substrate and the ZnO.

2. Experimental details

Two different kinds of synthesis techniques were used to grow ZnO nanostructures on the p-type substrates. The first technique were the vapor liquid solid (VLS) method, common used for growing ZnO [1]. In this method ZnO powder were mixed with graphite powder with a weight ratio of 1:1. The mixed powder was placed in a boat inside a tube furnace. The p-type substrate, coated with a thin Au-layer (1-5 nm) were placed on top of the powder with the Au-layer facing down with a powder-substrate distance of 3-5 mm. The growth temperature were 890°C for both the nanorods and nanodots growth. The growth time for the nanodots were 5s and for the nanorods the time were varied between 30-90 min. The other approach for growing ZnO were the aqueous chemical growth (ACG). In this method 0.025M zinc nitride (Zn(NO$_3$)$_2$6H$_2$O) were mixed with 0.025M HMT (C$_6$H$_{12}$N$_4$). The substrate were placed in the solution and everything were heated to 90°C for 90-180 min. For some samples a ZnO seed layer were used. The seed layer were produced by diluting 5 mM zinc acetate dihydrate in ethanol. A droplet of the solution were put in the p-type substrates, waited for 10 s and rinsed with clean ethanol. This coating step was repeated five times and then heated to 250°C in air for 20 min to yield layers of ZnO on the substrates. The zinc acetate deposition procedure was carried out twice to ensure a uniform ZnO seed layer. Details about this procedure can be found in [43].

After the synthesis; dielectric isolation was performed and top and bottom contacts were deposited and annealed. The insulating layer were spin coated on the substrates with a thickness around 200-500 nm. As dielectric isolation PMMA 4, 5 and 10 and photoresist AZ1450 were used. The bottom contact to the p-type Si was achieved using Al (110 nm), annealed in Ar ambient. While the top contact was performed using shadow mask with circular holes define the p-n heterojunction active device area employing Ti/Au (60 nm/40 nm). For the device using ZnO nanodots around 100 nm tin doped indium oxide (ITO), having 1.25 mm radius of circular geometry, was used as an optical window and current spreader on to the ZnO nano crystal layer. After depositing the ITO the samples were annealed at 450°C. The nanodots devices were fabricated with and without a 3 nm SiO$_2$ layer between the p-Si substrate and the ZnO dots. Figure 1(d) shows a schematic drawing of the devices.

The devices were characterized using scanning electron microscope (SEM), electroluminescence (EL) and current-voltage measurement (I-V).

3. Results

Our recent successful demonstration of high brightness white light emitting diodes are shown in Fig. 1, [44]. Figure 1(a) shows a image obtained from a digital camera of the light emission under forward bias. The EL spectra obtained under same condition is shown in 1(b). Figure 1(c) displays an encapsulated LED and (d) a schematic drawing of the processed device. These LEDs were grown with the ACG on p-SiC and the color temperature and color rendering index (CRI) of the LEDs values were measured. The results were (3250 K, 82), and (14000 K, 93), for the best LEDs, which means that the quality of light is better to the LEDs available on the market today. Figure 2 displays SEM images of ACG grown nanorods (a) with and (b) without the ZnO seed layer. By using this layer the growth result were improved, as seen in Fig. 2. The nanorods grown with the seed layer have smaller diameter then the nanorods grown without the seed, but the amount of nanorods was increased and the alignment was improved. The diameter of the seed layer grown nanorods were between 10-100 nm.

In Fig. 3 typical SEM images of ZnO nanocrystals under different stages of processing a LED are shown. Figure 3(a) shows the grown ZnO nanodots, their diameter varies between 20-100 nm. Nanorods after growth (b), coated with insulating layer (c) and after evaporation of the top contact (d) is also shown in Fig. 3. The hexagonal nature of the nanorods, seen in Fig. 2(a) and Fig. 3(b), are evident indicating high quality ZnO nanorods. It is important that parts of the nanorods are above the insulating layer, so that the top contact is connected to the
FIG. 1: (a) Digital image displaying the EL of a ZnO nanorods grown on p-SiC LED under forward bias for a diode having dimensions of 0.2mmx0.8mm. The measurements were performed through front to back biasing with current ranging from 10 mA up to 100 mA, (b) Electroluminescence spectrum obtained from the same sample at two different biases, (c) an encapsulated LED, and finally (d) a schematic drawing of the processed LEDs. From [44]

FIG. 2: Typical SEM images of ZnO nanorods grown on p-Si (a) with and (b) without the ZnO seed layer.

FIG. 3: SEM images from the different LED fabrications steps. (a) shows the ZnO nanodots as grown, (b) the as grown nanorods, (c) the nanorods coated with the insulating layer and finally (d) the sample after evaporation of the top contact.

The devices with buffer layer also showed EL emission under reverse bias. Typical spectra for the devices without the SiO$_2$ buffer layer under forward bias are shown in Fig. 5(a), with the buffer layer under forward bias in 5(b) and with the buffer layer under reverse bias in 5(c). In the case of forward bias the substrate was held positive potential with respect to top contact (or ITO optical window). Both devices had a detectable threshold voltage of around 3 V under forward bias condition. Current passing through devices under EL emission was between few hundred µA to few mA for the device without buffer layer. However, for the other device (device with buffer SiO$_2$ layer) the current was of the order of few tens of mA. Furthermore, in both devices there is an asymmetric EL emission peak at around 600 nm, see Fig. 5. The emission from the devices having buffer layer are a bit blue shifted when compared to samples without the buffer layer. The usual ZnO emission bands, i.e. the UV emission band and the DBE are not observed. However, the emission in Fig. 5 is close to the orange-red emission band usually attributed to O$_i$, see e.g. [45]. It might also be due to indium diffusion in to ZnO layer from ITO optical window. This needs further investigation.

It was observed that EL intensity saturates and then tends to decrease after some point. The saturation point of the devices with the buffer layer are higher compare to devices without the SiO$_2$ layer. Further, the maximum applied voltage for reliable operation of the devices is also different for the two kinds of ZnO nanodots devices. The reliable operation voltage for the devices without SiO$_2$ layer was between 2.5 to 8 V and after 10 V the
devices generally tends to sudden degradation with large amount of current. This is probably due to leaking or other breakdown mechanism (the main reason could be investigated with new set of different samples). The devices with the oxide layer could operate up to 30 V or more in a reliable manner. It seems that oxide layer also increases the efficiency of the devices. In the reverse bias both devices are inefficient compared to the forward biasing. In Fig. 5(c), the EL result of oxide buffered device is seen under reverse bias, the detectable EL threshold was generally around 12-14 volts, EL spectrum is almost same with forward bias case except additional emission around 450 nm at some bias voltage. The device without the buffer layer does not show any detectable EL spectra under reverse bias.

In summary, both ZnO nanorods and nanodots (with and without a oxide buffer layer) were grown on p-Si, forming p-n heterojunctions. The nanorods devices showed no EL emission but a rectifying behavior with a breakdown voltage around -4V. The nanodot devices showed EL emission under forward bias conditions. It seems that the buffer layer increased both the stability and efficiency of the devices, since the buffer layer device could operate at larger applied voltage and showed EL emission under reverse bias.

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