

Synthesis and Analysis of ZnO Nanorods using Molecular Beam Epitaxy

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Abstract

This paper presents a useful study on the synthesis and characterization of ZnO nanorods using (MBE). ZnO layers of thickness $\leq 500\text{nm}$ were grown on *p*-type silicon wafer Si (100) under conditions: substrate temperature 300°C , temperature of the Zn-Knudsen cell $\sim 286^\circ\text{C} \pm 0.5$, pressure of the chamber $\sim 4 \times 10^{-4} \pm 0.5 \times 10^{-4}$ mbar and oxygen plasma was generated by RF power supply operated at 300W. The as-grown ZnO layer was characterized by means of Fourier transform infrared (FTIR), scanning electron microscopy (SEM), Raman scattering and x-ray diffraction (XRD) and *I-V/C-V* measurements. FTIR displays a clear Zn-O bond at 406 cm^{-1} excitation, large area SEM image demonstrates well defined nanorods of length $\sim 100\text{ }\mu\text{m}$ while energy dispersive analysis x-ray spectrum (EDAX) reveals Zn-O at% as 56:44 that means the stoichiometric ratio is less than 1. Raman scattering exhibits nonpolar modes of Zn and O (sub-lattices) at 109 and 436 cm^{-1} respectively which clearly justifies the presence of nanocrystals/nanoparticles and in addition it also yields A1(LO) mode (polar) associated with ZnO. XRD pattern shows that the preferable direction of the growth of ZnO is along (0002) direction however additional peaks (weak) are also present. From the existing literature, useful discussion has been carried out to justify the obtained results and henceforth interesting conclusion has been drawn for device quality material.

Keywords: MBE; ZnO nanorods; FTIR; SEM; XRD; Raman scattering

1 Introduction

ZnO nanorods have potential as one of the most important candidates for next generation opto- and nanoelectronics [1]. However, synthesis of high quality and stable ZnO nanorods remains a challenge thus far [2].

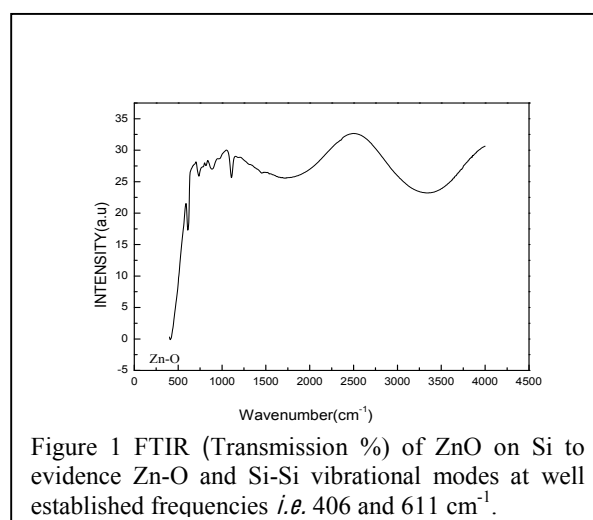


Figure 1 FTIR (Transmission %) of ZnO on Si to evidence Zn-O and Si-Si vibrational modes at well established frequencies *i.e.* 406 and 611 cm^{-1} .

Similarly fabrication of thermally stable and rectifying metal/nanorod-ZnO and Ohmic contacts also pose an uphill task. Furthermore, due to the presence of huge amount of interstitials and/or vacancies, ZnO has

intrinsically, *n*-type conductivity; as a result, it is difficult to dope it with *p*-type dopants [3]. Henceforth as way around such challenges, ZnO is being grown on friendly *p*-type substrates where GaN is more prominent. But, GaN itself is a costly material and therefore inexpensive templates are attracting the attention of the researchers for this goal. Various growth techniques are being attempted to grow improved quality ZnO nanorods but each of the method leaves defects in the form of vacancies and/or

interstitials in the layer. However, molecular beam epitaxy (MBE) because of its kinetic mode promises a better control and quality growth of the material.

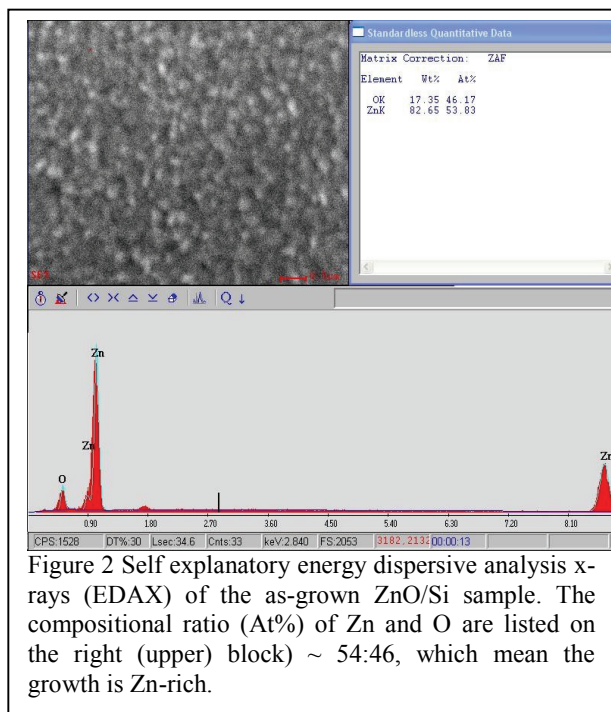


Figure 2 Self explanatory energy dispersive analysis x-rays (EDAX) of the as-grown ZnO/Si sample. The compositional ratio (At%) of Zn and O are listed on the right (upper) block) ~ 54:46, which mean the growth is Zn-rich.

In continuation with our preliminary results presented in the 'International Nanotechnology Conference for Industries INCI 2009 held at King Saud University Saudi Arabia [4], this paper presents a study on the synthesis and analysis of ZnO nanorods using molecular beam epitaxy (MBE). ZnO layers of thickness $\sim 1\mu\text{m}$ were grown on p-type silicon wafer Si(100) under conditions: substrate temperature 300 - 430°C, temperature of the Zn-Knudsen cell 300°C, pressure of the chamber 4×10^{-4} mbar and oxygen plasma was generated by RF power supply operated at 300W. The as-grown ZnO layers were characterized using Fourier transform infrared (FTIR), energy dispersive analysis x-rays (EDAX), atomic force microscopy (AFM) Raman and x-ray diffraction (XRD). FTIR displays a clear Zn-O bond at excitation 406 cm^{-1} , large area SEM image demonstrates well defined nanorods erected upwards while energy dispersive spectrum (EDAX) reveals Zn-O At% as 54:46 that means the stiochiometric ratio is less than 1. AFM confirms growth of nanorods however with the increase of thickness of the ZnO layers the rods are merged into bigger grains. XRD pattern shows that the preferable direction of the growth of ZnO is along (0002) direction which justifies the hexagonal structure of ZnO. Contrary to typical intrinsic carrier concentration of ZnO, the low value of the same ($\sim 10^{15}\text{ cm}^{-3}$) our sample reciprocates to the more quality ZnO layer. From the existing literature, useful discussion has been carried out to justify the obtained results and

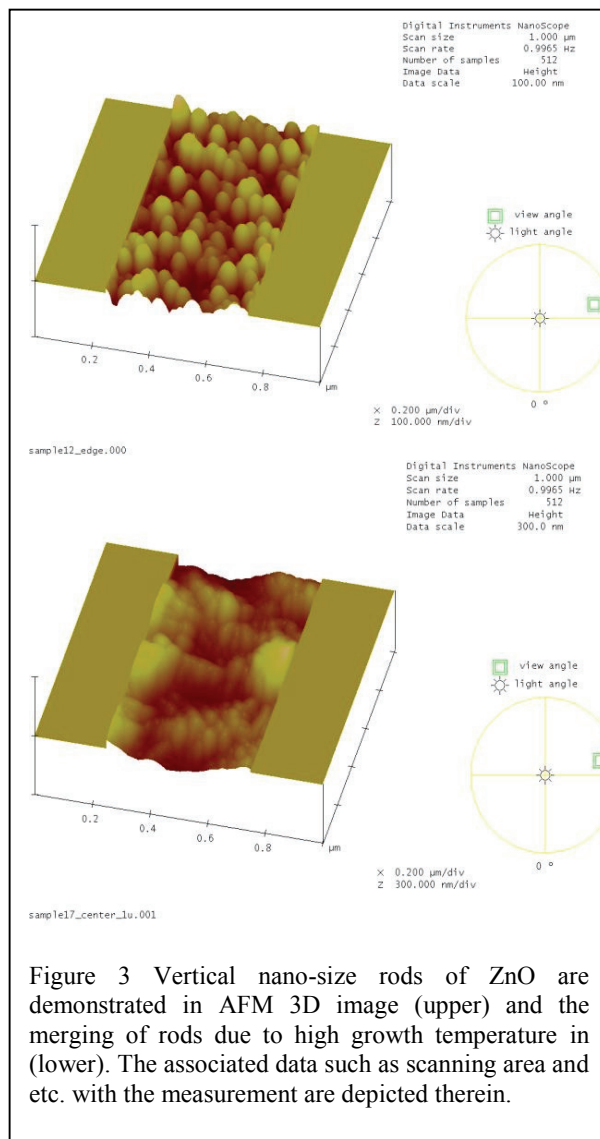


Figure 3 Vertical nano-size rods of ZnO are demonstrated in AFM 3D image (upper) and the merging of rods due to high growth temperature in (lower). The associated data such as scanning area and etc. with the measurement are depicted therein.

henceforth interesting conclusion has been drawn for device quality material. Experimental detail, results and discussion, and concluding remarks are described in sections II, III and IV, respectively.

2 Experimental

ZnO layers were grown on p-type silicon wafer Si(100) under conditions: substrate temperature 300°C - 430 °C, temperature of the Zn-Knudsen cell 300°C (Zn beads of purity 99.9999 were filled therein), pressure of the chamber during the growth was $\sim (1-4) \times 10^{-4}$ mbar and oxygen plasma was generated by RF power supply operated at 300W. Characterizations of the ZnO films were carried out with the help of following instruments/equipment: Tencor Alpha Step 200

Profilometer for Ellipsometry, Thermo Nicolet Nexus 870 FT-IR for FTIR measurement, PANalytical X'pert x-ray diffractometer (XRD) with Cu K α radiation source for XRD measurements, JEOLJSM-5910LV for SEM, Horiba Raman Spectrometer for Raman and 72AD Boonton Capacitance meter for C - V measurements and Keithley 617 Programmable Electrometer for I - V characteristics. For I - V and C - V measurements, Ohmic contacts on ZnO/Si (Ag/Ni 2000:200Å)/Al (2000Å) were deposited under standard conditions.

3 Results and Discussion

Ellipsometry of the as-grown layers at four different points of the wafer covered by the substrate holder were used to measure the thicknesses of the layer which were estimated to be in the range of 0.95 – 7.45 μm . The variation in the layer thickness is related with substrate temperature (300 – 430°C). Figure 1 demonstrates transmission FTIR spectra of as-deposited samples, where we can see three prominent peaks at 404, 611 and 1150 cm^{-1} . Peak appearing at 404 cm^{-1} is related well established excitation of vibrating Zn–O bond [5] and those at 611 and 1150 cm^{-1} are due to Si–Si and C–O bonds, respectively. SEM of the ZnO layer shows plane view of vertically aligned nanorods of ZnO (c.f. left upper figure 2) and energy dispersive analysis x-rays (EDAX)

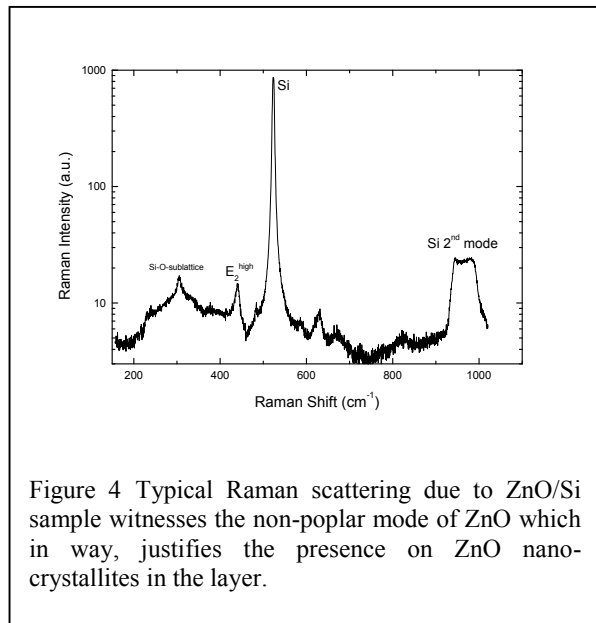


Figure 4 Typical Raman scattering due to ZnO/Si sample witnesses the non-polar mode of ZnO which in way, justifies the presence on ZnO nanocrystallites in the layer.

results indicate that Zn-O At% is as 54:46 that means the stoichiometric ratio is less than 1 and the growth is Zn-

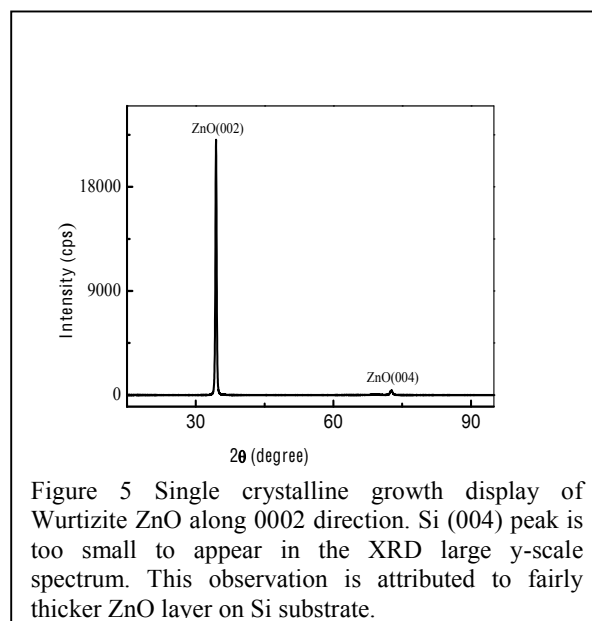


Figure 5 Single crystalline growth display of Wurtzite ZnO along 0002 direction. Si (004) peak is too small to appear in the XRD large y-scale spectrum. This observation is attributed to fairly thicker ZnO layer on Si substrate.

rich (see figure 2). As a matter of fact, the excess Zn contents are supposed to occupy O sites or interstitials to provide n -type conductivity of the layer (detail comes later). Figure 3 (upper and lower) display the AFM 3D pictures due to AFM measurements corresponding to thinner to thicker (0.95 to 7.45 μm) ZnO as grown layers respectively, where we can see that nanorods of size nearly 30 nm are vertically aligned but their grain size is increased due to merging process and eventually larger plateau like surface is developed. The plane view of the surface (1 $\mu\text{m} \times 100\text{nm}$) from AFM supports the SEM micrograph (not shown here). Figure 4 demonstrates Raman scattering exhibiting nonpolar mode of ZnO at 436 cm^{-1} which clearly justifies the presence of nanocrystals/nanoparticles and in addition it also yields A1(LO) mode (polar) associated with ZnO. Figure 5 depicts the XRD data of the ZnO/Si sample, where we can see that the preferential growth direction of ZnO is along (0002) *i.e.* along c -axis, in other word, this also means that Wurtzite ZnO has been grown on diamond Si. Since XRD spectra show only two peaks originating from ZnO: (0002), (0004) and Si (004) peak is too small to appear in the XRD large y-scale spectrum [6]. This observation is attributed to fairly thicker ZnO layer on Si substrate. Moreover, the single crystalline growth of hexagonal ZnO along 0002 direction is confirmed as well.

Typical C - V measurements on n -ZnO- p Si are shown in figure 6 which reveals a one-sided junction and the depth profile of the ZnO layer indicates that at the interface free electron will be depleted and therefore the profile ascends towards the bulk (neutral region). The free carrier concentration measured from these data is $1 \pm 0.5 \times 10^{15} \text{ cm}^{-3}$, the source of n -type conductivity is certainly due to the excess of Zn contents as pointed out by EDAX

data. Since the p -Si used for the substrate has hole concentration $1 \times 10^{17} \text{ cm}^{-3}$, this mean that about 90% of the depletion region should be in ZnO ($w_D \approx N_D/N_A$). This observation strengthens *Type II* heterojunction of ZnO/Si device as explained in figure 6. In this way, it is simply clear that we have succeeded to produce p - n junction on ZnO and Si, further studies will ascertain the optical properties of the device, reported elsewhere [7].

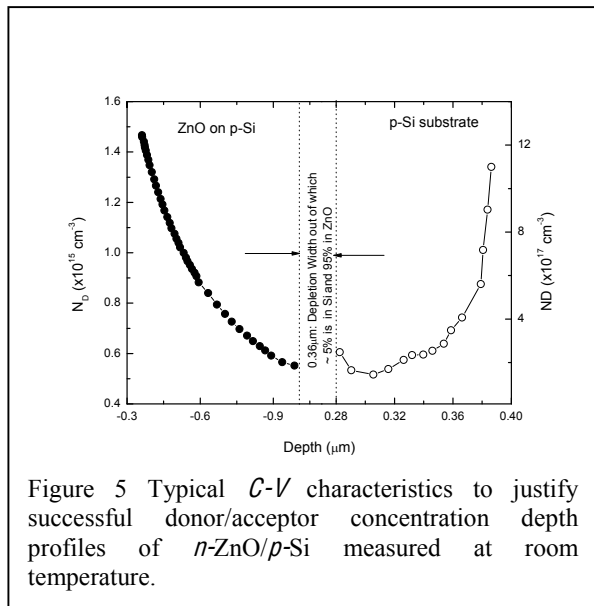


Figure 5 Typical C - V characteristics to justify successful donor/acceptor concentration depth profiles of n -ZnO/ p -Si measured at room temperature.

3 Concluding Remarks

ZnO was grown on p -Si (1 0 0) by means of MBE in order to characterize the properties of the p - n junction. Prior to making Ohmic contacts on the two materials, the as-grown layer was characterized using FTIR, SEM/EDAX, AFM Raman and XRD. FTIR showed a well defined Zn-O bond, AFM demonstrates the

formation of nanorods and their integration subject to the thickness of the ZnO layers and XRD revealed single crystalline Wurtzite structure of ZnO along 0002 direction. Raman scattering exhibits nonpolar mode of ZnO (sub-lattices) 436 cm^{-1} respectively which clearly justifies the presence of nanocrystals/nanoparticles. C - V measurements confirm the presence of *Type II* heterojunction between ZnO and Si where about 90% of the depletion width comes from ZnO.

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