Fabrication and characterization of p-type SiNW/n-type ZnO heterostructure for optoelectronics application

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Abstract: Semiconductor hybrid structure, known as core-shell heterostructures was fabricated and optical properties were analyzed to make it applicable in future optoelectronic and photonic devices. Large-area, high density, vertically oriented silicon nanowire arrays, synthesized by means of metal-assisted chemical etching of p-type silicon (100) substrate was used as the core and zinc oxide (ZnO) layer, deposited on the SiNW arrays by atomic layer deposition (ALD) was used as shell. The XRD peaks of the heterostructure confirmed the subsequent growth of ZnO film on the template of SiNW arrays having similar crystalline quality. The photoluminescence (PL) spectra showed a very sharp peak at 378 nm, corresponding to the band gap of ZnO material and another broad emission band almost throughout the entire visible range with a peak around 550 nm. The structure also showed a very good antireflection property. The results present that the SiNW/ZnO heterostructure can have potential application in future nanoscale electronic and photonic devices.

1. Introduction
In recent years, high-aspect ratio silicon nanowire based heterostructures attracting interest due to their potential application in broad areas, ranging from nanoelectronic, photonic to biomedical sensing applications [1,2] and their compatibility with present day Si based optoelectronic nano-devices and Si-integrated circuits. In present day optical industries, ZnO is considered as a promising material for applications including blue and ultraviolet optical devices, and gas sensing [3]. ZnO, a II-VI compound semiconductor having wurtzite crystal structure with wide and direct bandgap of ~3.37eV at room temperature and large exciton binding energy (60 meV) can prepare nanostructures with diversified morphology [3]. Um et al. for the first time reported radial heterojunction nanowires (NWs) using ZnO (shell)/Si (core) coaxial structure for a novel photodiode application [4]. They showed that the approach can promote surface enhanced electron-hole separation in ZnO nanostructure and the charge carrier separation in radial heterojunction which leads to the improvement in photosensitivity with spectral response enhancement. Although ZnO nanostructures as well as SiNW structures have been introduced in various previous studies to obtain a high conductivity gain with ZnO NWs [3] or strong light absorption with SiNWs [5], the investigation of properties of combined or heterojunction nature of these two is a relatively new field and needs more attention. In this paper SiNW/ZnO heterostructures were studied for their optoelectronic applications.

The fabrication of SiNW/ZnO heterostructure has to be done in two steps. In first stage SiNWs should be fabricated and the ZnO deposition on SiNW arrays should be done in second stage. There
are a number of techniques to produce Si-nanostructures. Currently SiNWs are produced by different methods such as laser ablation, thermal evaporation, chemical vapor deposition, chemical etching, and solution growth [6]. These techniques have their own limitations, as complex 3D shapes are difficult to produce and it is very hard to maintain high aspect ratio structures with varying degrees of complexity as feature sizes shrink into the nanoscale. Nevertheless, controllable and repeatable large-area SiNW array fabrication is still a problem. WE synthesized SiNWs on silicon wafer through a simple and conventional nanoelectrochemical etching technique without the use of a template near room temperature, as demonstrated by Kuiquing Peng et al. for the first time [5]. In this process, the simultaneous growth of metal dendrites accompanied with the etching of silicon wafer is a very important factor in the formation of nanostructures. Si nanostructures with different morphologies and properties can be produced by varying several parameters, such as, type of deposited metal (Pt, Ag, Au etc.), variation of etching time duration and temperature, concentration of etchants, wafer orientation and morphology of the metal film [7]. There is a lot of technique available also for ZnO deposition, such as pulsed laser deposition (PLD), atomic layer deposition (ALD), molecular beam epitaxy (MBE) and sol-gel method [3]. Among all the above described methods, ALD is the cost-effective and most promising method, which guarantees conformal deposition of ZnO film with extremely uniform and reproducible thickness, low stress and low defect density. Nanocrystal films are well suited for ALD, since their open structure allows diffusion of gaseous precursors, and thus allows an easy layer-by-layer filling of interstices. In this study, fabrication of SiNW/ZnO heterostructure was done by depositing of ZnO film on metal-assisted chemically etched SiNWs by atomic layer deposition method.

2. Experimental Details

2.1. Synthesis of SiNW
P-type, boron doped silicon (100) wafer was cut into small rectangular strips and properly cleaned. The growth of SiNW was achieved at atmospheric pressure and low temperature (50°C) using ultrasonication method. Analytical grade (99.99% pure) 4.6 mol/l hydrofluoric acid (HF) and 0.02 mol/l silver nitrate (AgNO₃) were mixed in teflon coated vessel and Si stripes were dipped in the solution for 1 hour for the etching purpose. The as grown SiNW substrates with clapped silver dendrite film were dipped in the 30 wt. % HNO₃ aqueous solution for removing the clapped silver. Then the samples were rinsed with de-ionized water, dried at oven, and subjected for further deposition.

2.2. ZnO deposition
After SiNW synthesis, ultrathin ZnO film was deposited onto as prepared SiNW by atomic layer deposition (ALD) technique (equipment model TFS 200 from BENEQ). In this process two precursors, diethylzinc [Zn(C₂H₅)₂, DEZN] and DI water were used as the source of zinc and oxygen respectively to produce ZnO with pulse duration of 100 ms each and the purging time of 1 sec. Nitrogen was used as both carrier gas and purging gas with flow rate 200 sccm. The substrate and precursor temperature was 150°C and 20°C respectively. The thickness of ZnO film was about 100 nm for 500 cycles of deposition. The microstructures of the films were analyzed by scanning electron microscope (SEM), atomic force microscope (AFM) on contact mode and X-ray diffraction spectra (Bruker D8 Advance XRD). Optical properties of the nanostructure templates were showing by photoluminescence spectra with a laser source with wavelength of 325 nm and a PerkinElmer Lambda 950 spectrophotometer.

3. Results and discussion
The surface morphology of the wafer-scale SiNW arrays before and after deposition of ZnO was studied by FESEM and AFM imaging. Figure [1(a)] shows that the as-prepared blank SiNWs formed bunches with average diameter and length of single nanowire varied around 200-500 nm and 6-8 µm respectively. The formation of nanowire is uniform and aligned vertically in a large area, also covering
the whole sample. The figure [1(b)] shows the 2-D AFM image of SiNWs coated with ZnO by ALD. The figure clearly depicts that the morphology of SiNWs remain intact after the deposition of ZnO.

![AFM Image](image1.png)

**Figure 1:** (a) SEM image of SiNW arrays, (b) 2D AFM image of ZnO film grown on SiNW arrays

XRD spectra in Figure [2] showed that the SiNWs had very good crystalline quality and predominantly having (002)-orientation with full-width at half-maximum of only 0.15°. Though, there were some other weak peaks, originating from other crystallographic planes. The spectrum also showed the polycrystalline nature of ZnO layer as grown on SINW template. Although the (002) peak at 2θ=34.45° with FWHM value of 0.7° was predominant in nature, indicating that most of the c-axis of ZnO grains were arranged perpendicular to the substrate surface. Indeed, the results ensured the subsequent grown of ZnO films were having similar crystalline quality as of the SiNW templates.

![XRD Pattern](image2.png)

**Figure 2:** $\theta$–$2\theta$ X-ray diffractogram of SiNW arrays (blue dashed line) and ZnO film deposited on SiNW arrays (red line)

After the detailed analyses of the microstructures, the point of discussion of our work is optical properties of the Si/ZnO core–shell nanowire arrays. In the PL spectrum shown in figure [3] shows two peaks. First of all there is a sharp peak at 378nm, corresponding to the band gap of ZnO (3.28 eV), presumably due to the direct electron-hole recombination across the intrinsic gap of ZnO [1]. There is also a broad spectrum, from 450 nm to 650 nm, centered at around 550 nm and covering almost the entire visible region, consistent with the previous reports [1, 2]. SiNW/ZnO heterojunction exhibits a type II core–shell band alignment based on Anderson’s model as shown in energy band diagram in Figure [4]. The conduction band minimum of ZnO is 0.34 eV higher than that of silicon. The electrons injected from ZnO into the neighboring one, to recombine with the holes in the valence band of silicon, responsible for the emission on 2.46 eV (~500 nm). Though this Type-I peak was very weak as the absorption depth of the excitation beam depends on the excitation source as well as the absorption coefficient of ZnO and the penetration depth of laser [8]. A comparatively strong peak at 550 nm (~2.25 eV) was induced due to the Type-II defect present in ZnO because of the deep level
states in ZnO induced by various impurities and those defects which existed close to the valence band maximum of silicon. Here the holes in p-Si can tunnel into ZnO and may be trapped at deep level states in ZnO, resulting in the green emission [8]. Hence, devices based on a n-ZnO/p-Si heterostructure can emit green and red light simultaneously. The weak PL peak ranging from 450 nm to 650 nm originated from the trap state emission in ZnO might be detected due to the low quality of the interface between Si and ZnO [2]. The very good antireflection property of the device (in the order of 0.2% to 2.6% for the wavelength ranging from 300 to 900 nm) may also contribute some significant impacts to the marked enhancement of the observed visible PL emissions.

4. Conclusion
A simple method for the preparation of high aspect ratio quasi one dimensional SiNW-ZnO core-shell nanowire arrays is reported. Here conformal deposition of ZnO was done on metal-assisted chemically etched highly-ordered vertical SiNW by ALD technique. The detailed study of structural and optical properties of core-shell SiNW/ZnO heterostructure is represented through FESEM, AFM, PL and reflectometry analyses. The Si/ ZnO core-shell nanowire arrays can perform simultaneously in dual band of the spectrum namely ultraviolet and visible region respectively. The high aspect ratio, anti-reflective characteristics inherent to nanowire structure can be exploited for fabricating future nanoelectronic and optoelectronic devices.

Acknowledgement
The authors are deeply thankful to Laser Materials Processing Division, DAE-RRCAT, Indore for availing facilities to complete a part of the above project. They are also thankful to UGC-DAE CSR Centre, Indore for availing some of the characterization facilities.

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Figure 3: Photoluminescence spectra of SiNW/ZnO heterostructure at room temperature

Figure 4: Anderson’s model of band diagram of SiNW/ZnO heterostructure