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Semiconductor Nanowire based CMOS Compatible Field-Effect Transistor Biosensors for Ultrasensitive Detection of Biological Species

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Abstract: The ability to optically, electrically and magnetically detect the state of biological systems and species is continually being researched. Even though optical & magnetic procedures continue to grow and evolve, electrical detection methods, by-far, continue to remain most desirable. Nanowires (NW) have emerged as powerful platforms for creating robust, sensitive and selective sensors for biological detection. These NWs have been custom created & modified to be used for electrochemical biosensing, owing to their miniaturizing properties and effective recognition abilities. This paper specifically deals with the study of common and technologically relevant semiconductor materials, primarily Silicon (Si) & Zinc Oxide (ZnO), which have currently become the face of interdisciplinary bio-electrochemical research. The effect of thermal annealing as well as surface defect passivation on electrical transport properties for highly selective pathogen sensing has been discussed. Crystal optical and electronic characteristics of SiNW and ZnO based sensing channels have been observed to offer promising prospects in the discipline of Complimentary Metal-Oxide Semiconductor (CMOS) compatible Field-Effect Transistor (FET) biosensing. Operations such as drug discovery and pathogen detection by the means of semiconductor NW devices have been reviewed.

Keywords: Biosensor; Nanowire; Electrochemical; FET

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1. Introduction

Nanostructures, such as those of nanowires (NWs) [1] offer potential for new and advanced opportunities to produce highly selective and specific sensors. The diameters of these nanomaterials are comparable to those of the biological and chemical species being sensed. Ergo, they represent excellent primary transducers for producing signals that ultimately interface to macroscopic instruments. The combination of tunable conducting properties of semiconducting NWs and their ability to bind analytes on their very surface yields direct, label-free electrical readout, which is exceptionally attractive for many applications [4]. In addition these NWs also are known to exhibit highly reproducible electrical and optical properties. We discuss in this paper, various illustrative examples which demonstrate the multi-modal ability of such NWs in detecting such biological and chemical species, thereby providing a clear pathway for diverse and exciting biomedical applications.

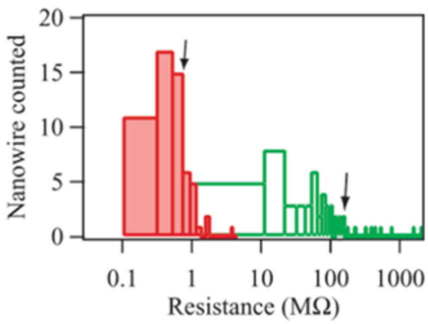
2. Silicon Nanowires - Structural Properties & Characterization

Semiconductor NWs (SiNW) composed of silicon have now taken up a significant step in being perhaps one of the most desired biosensing tools in the world. SiNWs can be easily prepared as single-crystal structures with diameters as small as 2-3 nm [2]. They can be prepared as p- or n-type materials and be configured as FETs that exhibit electrical performance characteristics comparable to or better than those achieved in microelectronics industry for planar devices. Also, the high-performance switching characteristics of SiNWs are among the most important factors that affect its sensitivity.

2.1. Effect of Thermal Annealing on Transport Characteristics

It is, in general, a known fact that Titanium (Ti) can form a stable conducting silicide with a low Schottcky barrier height on p-type silicon. Studies demonstrate that with thermal annealing, the $I\text{-}V_{sd}$ plots become more linear and symmetric, the transport behavior becomes stable and the conductance increases 3-fold [3]. Such measurements were made over 50 SiNW based devices. The results thus obtained, were summarized in a histogram as shown in Figure 1. Before annealing, the resistance shows a large distribution ranging from <MΩ to >GΩ with an average of 160 MΩ. In contrast, the resistance after annealing has a narrower distribution of 0.1 to 10 MΩ with an average of 0.62 MΩ. Thus, a 260x betterment in the two-terminal conductance is observed.

Figure 1. Histogram of Ti-contacted SiNW resistance determined from measurements before (open green bars) and after (solid red bars) contact annealing. Arrows fix average.

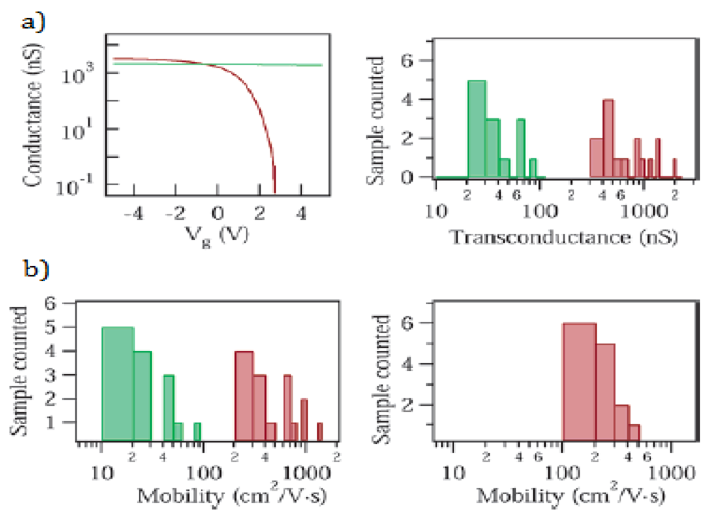


2.2. Surface Defect Passivation & effects on Transport Characteristics

Surface modification was carried out by reaction with 4-nitrophenyl octadecanoate, since it leads to a stable and relatively nonpolar Si-O-C ester linkage [5]. Post this, conductance i.e. I/V_{sd} vs. backgate voltage (V_g) measurements were performed and results were obtained.

As is evident from Figure 2, the conductance of a normal device without surface defect passivation, responds poorly to V_g. In contrast, the conductance is extremely sensitive to V_g after modification and can be effectively shut off at V_g ~ 2.5V with an on/off ratio over 4 orders of magnitude, which invariably is an order of magnitude larger than before modification. Moreover, the mobility of holes in the SiNW is also estimated after modification, using a cylinder on an infinite plate model. It is assessed at 1000cm^2/Vs which is substantially larger than that obtained in conventional Si devices.

Figure 2. a) Conductance vs V_g measured on the same SiNW before and after surface defect modification. Histogram for cumulative results is also plotted. b) Mobility plots thru histograms for before and after surface defect passivation with 4-nitrophenyl octadecanoate



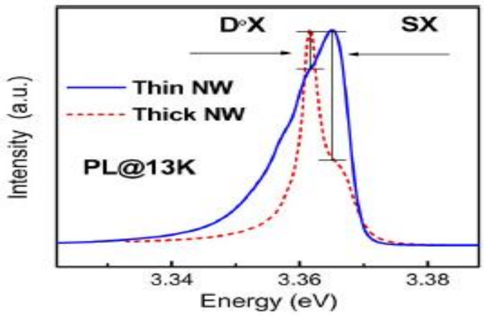
3. Zinc Oxide NW based Electro-chemical Biosensing

Being amongst the II-VI semiconductors, Zinc Oxide NWs (ZnO NWs) have been extensively studied for their abundant physical properties and versatile device applications. Being a polarized semiconductor, it exhibits strong piezoelectric properties and has a direct wide bandgap of 3.37 eV at room temperature, coupled with a larger exciton binding energy of 60 meV that ensures efficient exciton emissions at room temperature. In addition to this, its small size is very much comparable to its Debye length, which makes ZnO NWs superior chemical adsorbents.

3.1. Optical Properties

For ZnO NWs, band edge emission peak is observed at ~3.37 eV. The results obtained from PL spectroscopy of different NWs with different dimensions have been compared in Figure 3. Thick NWs of ~200 nm diameters, characterized by dashed lines, show a strong peak at 3.362 eV. This is primarily due to the emission of donor-bound excitons from the NW surface, when exposed to light (D°X). In contrast, the spectrum of thinner NWs i.e. of ~15nm, with plot characterized by a solid blue line, shows a shift of the dominant emission peak to 3.366 eV, due to the emission of surface-bound excitons from the NW during PL spectroscopy, due to an enhanced surface-to-volume ratio. This kind of large exciton energy merits ZnO as a prominent material for short wavelength optoelectronic applications.

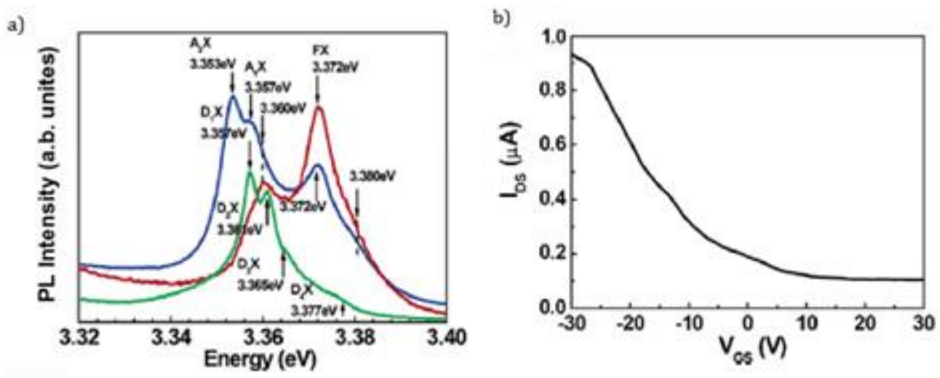
Figure 3. Band-edge emissions of ZnO NWs of small diameters show dominant surface bound exciton peak SX contributing to a blue shift in the PL spectra.



3.2. Doping of ZnO NWs

Recently, introducing Phosphor (P), as the extrinsic acceptor has been termed as a successful method in bringing about p-type characteristics in ZnO NWs. Phosphorus Pentoxide (P_2O_5) is used as a dopant source mixed with ZnO/Graphite powder, and synthesized P doped ZnO in a CVD process. Following an annealing process, ZnO NWs demonstrate p-type conduction behavior, which is confirmed by the evolution of acceptor-bound exciton (AX) peaks in PL measurement, in contrast to the attenuation of donor-bound (DX) and free exciton (FX) peaks [Figure 4 a)]. Further, the I_{ds}-V_{ds} & I_{ds}-V_g characteristics were also plotted as in Figure 4 b). Applying a negative value of gate voltage to the FET device enhances the conductance of the NW and further aids the p-type behavior.

Figure 4. a) The PL spectra of a nondoped NW (green) doped NW before annealing (red) and (blue) doped after annealing. b) p-type I_{ds}-V_g curves of NW after annealing.



4. Applications in Medical Diagnostics

To configure NW sensors and enable them to selectively screen inhibitors in drug delivery, Ab1 tyrosine kinase was linked to the surface of the SiNW FET and the binding of ATP and competitive inhibition of ATP binding with organic molecules, such as the drug Gleevec was studied [6]. Data recorded from the Ab1-modified p-SiNW devices showed, concentration-dependent increases in conductance upon the introduction of ATP solutions, as illustrated in Figure 5 (a & b). Notably, the conductance is a pure function of the small-molecule concentration and depends strongly on the same. The studies demonstrate the strong advantages of NW detectors over existing methods for rapid, direct and high-sensitivity analysis of organic molecules using minimal amount of protein receptor.

Further, the ability of SiNWs to detect singular virular entities was studied. When a virus particle binds itself to the receptor probe on the NW device, the conductance of the device switches from its underlying baseline value. Similarly, as soon as the virus pathogen leaves the surface of the NW channel, the conductance again begins to regain its initial state [6]. This has been illustrated in Figure 6 via the attachment of a charged influenza pathogen to the NW interface.

Figure 5. a) Time-dependent conductance G curve at different ATP concentrations for a NW modified with the kinase Ab1. Regions 1, 2 and 3 correspond to 0.1, 3 and 20 Nm ATP respectively. Arrows indicate the points where the solution was changed. b) ΔG vs ATP concentration for an Ab1-modified SiNW (red) and a SiNW without Ab1 (black).

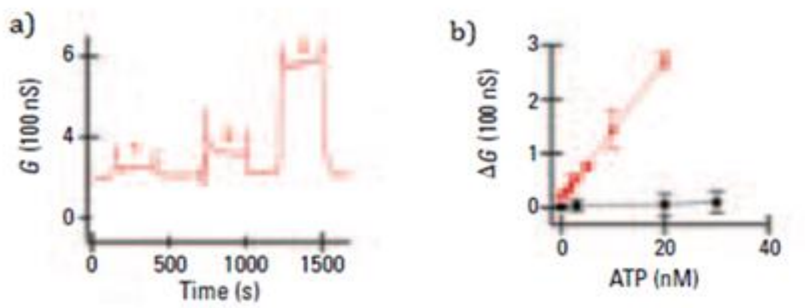
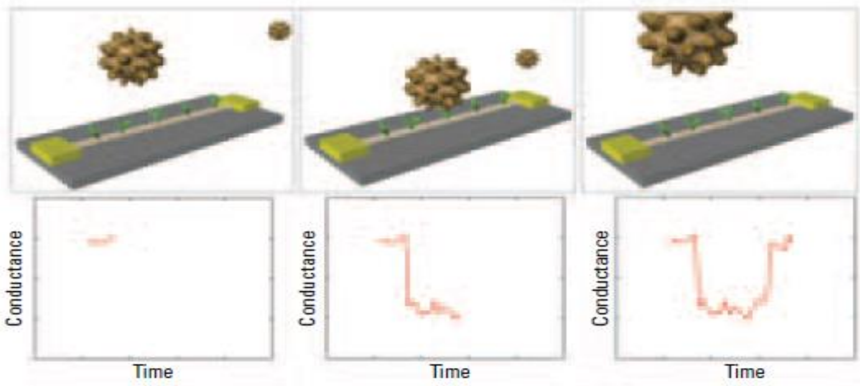


Figure 6. Schematic of a single virus particle binding to and unbinding from the surface of a SiNW device that was modified with antibody receptors. Respective conductance change has also been shown.



5. Conclusion

It is evident now that, semiconducting NW based FET biosensors enriched with receptor probe molecules to enhance their specificity, represent perhaps one of the most powerful systems in the world of electrochemical based biological detection today. A multitude of biological, chemical and foreign bio-organisms can coherently be detected by the means of these biological sensor devices. Moreover, such NW based sensors offer real-time detection as well as transduction of the output electrical signals all integrated into one single package, thereby widening the scope for next-gen disease diagnostics. However, in spite of all this it should be noted that there still exists large scale scope for betterment in the various inherent properties of these materials. Further, these advances could be developed at the commercial level as well, in simple NW sensor devices that would represent a lucid application of nanotechnology. NWs can be very well integrated into a variety of devices and tools proving to be indispensable elements for the biomedical industry. Moreover, the possibility of incorporating both chemical and biological surface binding reactions into quantifiable electrical output signals itself suggest the potential of these NWs for highly sophisticated interface between nanoelectronic and biological information processing systems.

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Conflicts of Interest

The authors declare no conflict of interest.

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