Chapter

Prologue: Nanorods – Recent Advances and Future Perspective

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1. Introduction

Nanorods (NRs) are a one-dimensional wonder in the nanomaterials science which have shown promising future for its applications in many fields ranging from household appliances [1] to medical technology [2, 3] to space technology [4]. Nanosized materials with an aspect ratio (defined as the ratio of the length to the diameter of the NR) greater than 10 are considered as nanorods. With respect to other nanostructures, they present several advantages, like a larger surface-area-to-volume ratio, a direct carrier conduction path, a large variety of potential novel properties available through the control of size and structure, and high compatibility with standard industrial device fabrication technologies. Such structures are of particular interest to the researchers; we can see from the increasing number of papers, as they exhibit quantum confinement in two dimensions, while the third is relatively unrestricted [5] (**Figure 1**).

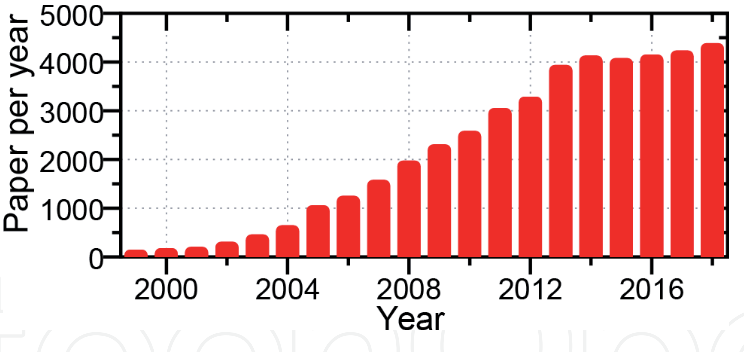

Figure 1.
Increase in the number of publication on the topic on nanorods for the last 20 years (Keywords: "Nanorods"; Source: Scopus).

2. Synthesis methods of nanorods

Nanorods can be grown by using either a *bottom-up* approach or a *top-down* approach. The *bottom-up* approach is the well-explored techniques, and varieties of NRs have been synthesized ranging from elemental metallic, organic, and semiconducting NRs and some complex oxide NRs. The chemical vapor deposition (CVD) is the most used and developed technique to synthesize various metallic, organic, and semiconductor NRs with controllable size and orientation based on a *bottom-up* approach. Control of size (diameter and length) of the NRs and its orientation on the substrate are achieved after extensive research on the growth of NRs by several researchers worldwide. However, it needs precise control of each of the growth parameters, e.g., source of the vapor, vaporization temperature, growth temperature, vapor partial pressure, catalyst size, etc. to prepare high-quality NRs with preferable size and orientation. There are intense review articles dedicated to the growth of NRs available for further reading. Fortuna et al. [6] presented an in-depth review on the control of growth direction of metal catalyst-assisted synthesis of semiconductor NRs. The key parameters for the radial and axial heterostructures growth and their potential uses in the electronic industry are well summarized by Lu et al. [7].

Another bottom-up approach is chemical synthesis technique to prepare metallic and semiconducting NRs. In this technique, the key component is the cationic surfactant chemical used in the solution mixture which restricts the nucleation in two dimensions. As a result, the nucleation/crystallization process takes place only in one dimension, and hence one-dimensional nanostructures are formed. For example, in the case of ZnO NRs, the most commonly used surfactant is hexamethylenetetramine (HMT). HMT in aqueous solution acts as a bidentate ligand and is capable of bridging zinc(II) ions in solution with another zinc(II) ions available only in the ZnO(002) facet. As a result, ZnO NRs preferentially grow along (002) direction. A comprehensive review of the growth mechanism and the role of HMT with different chemical precursors for the growth of the ZnO NRs are presented by Xu et al. [8]. Several factors influencing the size, morphology, and orientation of the epitaxial ZnO NRs on the solution using the hydrothermal method and tuning of their size and morphology are extensively discussed by Guo et al. [9]. Compared to the CVD technique, the chemical synthesis route is beneficial due to the comparatively low growth temperature, high throughput, and lower production cost. However, the quality of the NRs in terms of crystallinity, presence of defects, and properties, grown in the CVD method, is always much better than in the case of NRs grown by chemical route.

Assembly and integration of highly ordered NR arrays on a large scale are essential for multifunctional devices and systems. Large-scale production of NR array has been achieved by using both the CVD technique and chemical route using a pre-patterned seed layer. Recently, there is a report on the growth of high-yield nanowires/NR arrays by Wei et al. [10]. In this work, they demonstrated an effective approach for controllable wafer-scale fabrication of ZnO NR arrays by combining laser interference lithographic patterning and hydrothermal growth. Laser interference patterning is employed to control the position, size, and orientation of synthesized ZnO NRs, while a hydrothermal chemical method is used to control the morphology and material properties of NRs.

In the top-down approaches, reactive ion etching (RIE) and metal-assisted chemical etching (MACE) are well-developed techniques to grow vertically aligned NRs in a large scale. RIE involves dry etching of Si or SiO_2 by halogen radicals to grow a vertical array of Si NRs with different aspect ratios [11]. Solution-based MACE technique has recently emerged as an effective tool for rapid synthesis of vertically aligned high-yield NRs in a large scale [12]. A noble metal nanoparticle is used as a catalyst to start the growth of the NRs. The shape and size, density, and quality of the NRs are controlled by several parameters: (i) the size and shape of the metal nanoparticles, (ii) intermediate distance between the nanoparticles, (iii) etching parameters (concentration and temperature of the etching solution, and etching time duration), and (iv) crystal quality and orientation of the starting wafer [13]. Both the above-mentioned processes are generally anisotropic, and the use of a protective layer/masking is very important to get uniform NRs.

3. Emerging device applications of nanorods

Based on the several fascinating properties of the NRs which are observed only in the nanoscale regime, researchers successfully fabricated and demonstrated various prototype devices using NRs. Some of the important recent developments of device applications of NRs are summarized below.

The first step toward the application of any nanomaterials in the electronic industry requires the successful fabrication of transistor with efficient device performance. NRs from different materials ranging from elementary Si to oxide semiconductors to carbon have been successfully exploited in the field effect transistor (FET) devices [1]. So far, the highest mobility of 200 cm^2/V.s has been recently achieved from amorphous zinc oxynitride thin film [14]. Gluschke et al. [15] recently demonstrated a new fabrication method for high-quality gate-all-around TFT structure with independent top and bottom gate lengths. This approach overcomes significant limitations that exist in the wrap-gated NR transistors and the subthreshold swings achieved by this method as low as 38 mV/dec at 77 K for a 150 nm gate length TFT.

NRs have been successfully utilized as a light source by fabricating light-emitting diodes (LEDs) and nanolasers using NRs. There are many reports available where single-color-emitting NR-based LEDs were successfully demonstrated. Recently, core-shell InGaN/GaN NR-based LEDs are investigated for multiband emission. The emission of this LED covers nearly the whole visible region including UV. Emitted wavelengths and intensities are governed by different thicknesses of the InGaN/GaN grown on different crystal facets of the NRs as well as corresponding polarization-induced electric fields. For demonstration of the semiconductor NR laser with high-quality factor, a perfectly vertical orientation and smooth sidewall of the NRs are very important and crucial. From theoretical studies, it is found that the quality factor of the NR laser reduces to one third for a change in the inclination angle of the NRs of one degree (90–89°). Hsu et al. [16] developed an ultraviolet (~365 nm) GaN/Al metal laser that operates at room temperature with a low threshold power density of 5.2 mJ/cm^2. High-quality factor surface plasmon resonance (SPR) modes were achieved by incorporating an additional wet-chemical etching step with potassium hydroxide during the fabrication process. This step created nanorods with very smooth and vertically straight sidewalls that are truly perpendicular to the substrate.

Digital recording of data using light pulse instead of using magnetic field is recently explored by several researchers. The use of metal NRs for the data recording, instead of commonly used magnetic thin films, is realized. Zijlstra et al. [17] succeed to achieve five-dimensional optical recording in gold NRs by spectral and polarization multiplexing in single data bits with metallic nanoparticles for the first time. The gold NRs immersed in the polymer are used in this experiment for their unique SPR effect, and recording was done using a single laser pulse at femtosecond intervals. A DVD-size disk of three layers of gold NRs can hold 1.6 terabytes of information. This recording technology would revolutionize the optical storage industry with further miniaturization of storage devices.

Another important application of NRs is sensing, and varieties of NR-based sensors have been developed to date. In order to improve the sensitivity and time response of the NR-based light sensors, semiconducting NRs, mainly oxides, are exploited by fabricating inorganic-inorganic, inorganic-organic heterostructures, surface roughening, plasma treatment, and doping [18]. The present NR-based light sensors can compete with the existing Si-based thin-film sensors, and few of them are commercially available. A huge amount of work has been done on the NRs for the development of highly sensitive gas sensors for household/industry use and biosensors for the medical applications. So far, various oxide NRs have been utilized for the development of gas sensors which can detect H_2, CO, H_2S, methanol, acetone, and LPG gases with the sensitivity level down to 0.1 ppm [19]. Yasui et al. [2] developed a sensor composed of ZnO NRs anchored into a microfluidic substrate and demonstrated a noninvasive early detection of cancer-affected urinary micro-RNA. This technology moves researchers toward the goal of micro-RNA-based noninvasive and simple early cancer diagnoses and timely medical treatment.

NRs also provide an environment-friendly solution to the increasing global demand for energy. NR-based junction solar cells or dye-sensitized solar cells show promising energy conversion efficiency with a long life span. So far, the highest conversion efficiency of 17.8% was reported using InP NRs [20]. ZnO NRs can also be used as a nanogenerator to produce energy by converting mechanical energy to electrical energy (piezoelectricity) due to its nonsymmetrical crystal structure [21]. Furthermore, this technology can be integrated with any nanoelectronic devices/sensors for the development of self-powered wearable electronics.

4. Conclusions and perspectives

Now, NRs can be synthesized in a large scale in *top-down* approach as well as in *bottom-up* approach. For device fabrication, patterning of the substrate is very important, and a low-cost effective pattering technique is yet to develop. So far, many breakthroughs in terms of fascinating properties of the NRs and emerging devices have been achieved after extensive research in the past decade. Now we acquired knowledge of the pros and cons of using NRs for various applications. Many startups are working on commercialization of NR-based devices and successfully brought few such technologies into the market.

In most cases, higher sensitivity and stability were achieved from the devices made with NR heterostructures. The synergistic performance lies in the selection of right materials and the structural quality at the interface of the heterostructures. There is always a scope to improve further by finding a perfectly matched external material and a methodology for an easy formation of the high-quality guest-host interface. There is a huge demand for an environment-friendly technology for the energy-efficient white light source. NRs may fulfill this societal requirement, and to do this, we can realize a core-shell structure with composite oxide NRs or a combination of selective doping and formation of the homojunction.

Further intensive research on designed syntheses and easy nanofabrication of NRs for the large-scale device applications would provide an enormous impact on nanotechnology and open an unprecedented avenue in energy, magnetic, electronic, and spintronic applications. However, the future of NR technology will be dependent on how we can minimize the production cost by maintaining high efficiency and long stability of the devices.

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