



III-nitride nanowires for solar light harvesting: A review

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ABSTRACT

The world needs economical and sustainable alternate energy sources to combat the irreversible phenomenon like global warming. Solar photovoltaic technology, which converts sunlight directly to electricity, is the most potential candidate for alternate energy source. On the other hand, increasing global pollution due to energy emission compels the worldwide researcher community to deliberate over various green fuels. Recently due to numerous advancements hydrogen fuel cells are thought to be the green power source of 21st century and may develop the hydrogen economy. However, despite of many promising breakthroughs energy production harvesting solar light does not find wide spread applications due to their low efficiency associated with unsuccessful utilization of entire solar spectrum which leads researchers to consider materials with multi energy band gap. Due to their unique property of band gap tuning (~6.2 eV for AlN to ~0.65 eV for InN) III-nitride nanowire structures have been extensively investigated in the past decade in pursuit of multi band gap materials. Intensive research efforts have been paid into studying GaN, InN, InGaN, AlN and their different compositions. It is clear that this material family has enormous potential in harvesting solar energy to light the new dawn of clean and sustainable energy sources. In this article, we present an overview on recent advancements in III-nitride solar energy devices. We have made a review for more than 200 articles in this regard. All the recent developments in realizing III-nitride nanostructures and novel yet recent advances in III-nitride solar devices are reviewed in Section 2 and its subsequent subsections. The III-nitride nanowire photovoltaic devices are discussed in Section 3 whereas Section 4 deals with the current progresses in artificial photosynthesis involving III-nitride nanowires. Finally in Section 5 the present challenges in realizing high efficiency III-nitride nanowire solar energy devices are summarized along with paths for future work.

1. Introduction

In 2013 it is estimated that the global energy demand will exceed 30 TW which is double the current value [1]. This deadlock popular as the TerraWatt challenge is the primary concern of many strategic and environmental committees across the world. Rising challenges over anthropogenic climate change, energy security and resource availability (“peak energy”) have increased research interest of many to work in renewable energy sources such as solar cells, fuel cells, biomass, wind, geothermal, hydroelectric etc [2]. One of the most promising alternate energy sources is photovoltaic. Though photovoltaics have enormous potential of becoming a major contributor as alternative energy source, the real life application of it is small till date (< 1% of global energy supply) [2]. Factors like low efficiency, low energy density and relatively high cost constraint the wide spread application of photovoltaics. On the other hand, hydrogen fuel cells are thought to be the green power source of 21st century and may develop the hydrogen

economy. Increasing global pollution from energy emissions is the key motivation for researchers across the globe to work on this technology [3]. On the face of this pollution problem, hydrogen fuel cells offer energy production with zero emission while exploiting hydrogen as the fuel and air as the oxidant. This technology also displays better power density and efficiency over others in high power demanding areas such as electronic applications [4,5]. But the principal factor limiting the well spread usage of hydrogen fuel cells is impurity in hydrogen fuel such as CO, H₂S, NH₃ or other hydrocarbons. These impurities cause serious degradation in device performance and sometimes permanent damages [6,7].

One of the major points to be enhanced in terms of photovoltaics operations is the power conversion efficiency (PCE) of a device. PCE is the efficiency by which sunlight can be converted into electrical power. A significant research effort has been devoted to improving this efficiency while reducing the production cost. The first generation solar cells which is a single p-n junction realized on single crystalline or poly-

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crystalline Si substrate, share a vast majority of today's photovoltaics market [8,9]. But the production cost of this technology is high. Second generation solar cells also known as thin film cells are believed to cut down the production cost by using less material and low-cost substrates like metal foils, plastics or glass instead of single or poly crystalline Si [10,11]. This generation cells are largely fabricated with amorphous Si, cadmium telluride (CdTe) or copper indium gallium diselenide (CIGS) as the absorber layer [12–14]. All the before mentioned materials are of lower material quality which results to lower device efficiency than crystalline Si solar cells. Currently third generation solar cells [15] are being chased to meet the Shockley-Queisser efficiency limit [16] while simultaneously reducing the production cost. The highest recorded efficiency in this category of solar cells comes from III-V cells which was realized by employing highly perfect thin films of III-V group semiconductor having a multi-junction device structure [17]. These cells can absorb a wider wavelength which is the pivotal reason of their high efficiency of about 38.8% [18]. This is highest reported efficiency of any PV technology. However, these cells also face high processing cost concern. Currently extensive research activities have been pursued by numerous groups to overcome this processing cost problem by reducing active area with a low cost focusing optics [19]. Since the first report of the Honda-Fujishima effect in early 1970s [20], photocatalytic and photoelectrochemical (PEC) water splitting on semiconductor materials have been studied vigorously. But as has been discussed by many, the reported efficiencies are too low for real life applications [21,22]. To answer this challenge, many research groups employed a strategy to construct a novel morphology and structures of existing materials and compositions [23,24]. In this quest of finding new materials and new compositions of existing materials, III-nitrides find their obvious spots because of astonishing properties like wide ranged direct band gap (ranging from deep UV AlN (~6.01 eV) to far infrared InN (~0.7 eV)), high thermal stability and high electron mobility than Si [25–30]. One of the primary limitations towards wide spread usage of multi-band gap solar cells, is the realization of suitable multiple band gap materials which can be deposited easily despite having lattice mismatch parameters. III-nitride materials especially InGaN can potentially be an alternative replacing metamorphic materials which are now being used. III-nitride material family can cover almost all of the usable solar emission range (0.5–3.0 eV) due to their unique property of band gap tuning which can be achieved by varying composition (ratio of indium, x to gallium, $1-x$). Just by changing the composition the band gap of InGaN can be tuned from 0.7 eV (InN; $x=1$) to 3.4 eV (GaN; $x=0$) which spans nearly the entire solar spectrum. The band gap (E_g) has been determined employing the composition-weighted average of the GaN and InN gaps using a “bowing” parameter, b of 1.4 as following

$$E_g(x) = xE_g(\text{InN}) + (1-x)E_g(\text{GaN}) - bx(1-x) \quad (1)$$

However, most of the before mentioned approaches to meet the efficiency and materials concerns have been focused towards highly developed thin films of III-nitride materials. But, presence of extremely large defect densities still significantly limits the performance and applications of III-nitride planar devices. Therefore substantial efforts have also been devoted to realize III-nitride nanowires to fully exploit the potential of these materials [31–33]. The possibility of realizing a single crystalline nanostructure by employing simple and low cost growth technique lures many to research on nanowires. Moreover, a broad range of material combinations can be incorporated while growing because generally in nanowire synthesis process the dislocation due to lattice mismatch can be prevented. Therefore, due to elastic relaxation of the nanowires, greater lattice mismatch can be achieved through a pseudomorphic growth without defect introduction when compared to traditional two-dimensional thin film growth. Furthermore, nanowires show some extremely interesting electronic properties due to their quasi one-dimensional structure. Furthermore, the III-nitride nanowires can significantly scale down the future devices due to their reduced dimensions.

In this paper, we review the recent progress made in GaN nanowire optoelectronic devices to harvest solar light applications like photovoltaics and PEC. In Section 2, we discuss about the various growth/synthesis schemes to realize GaN nanowires. Also in this section we put an effort to understand their fundamental properties which in a way determine the overall efficiency of the devices. Applications of nanowires in photovoltaics and PEC are discussed in Sections 3 and 4. Finally, the summary and future prospects are presented in Section 5.

2. Growth and recent advancements of III-nitride nanowire technology

Various approaches to fabricate III-nitride nanowires are discussed in this section. Advances made to understand some fundamental properties which affect the overall efficiency of a device, is then presented. The first report of GaN was published by Maruska and Tietjen in 1969 [34]. The synthesis was carried out at Radio Corporation of America Laboratories (Princeton, New Jersey, USA) using a hydride vapor-phase epitaxy process on sapphire substrate. Since then, enormous work has been routed to developing GaN based optoelectronic and electronic devices. Prof. I. Akasaki, Prof. H. Amano and Prof. S. Nakamura have been awarded the Nobel Prize in Physics for their work on GaN based blue light emitting diodes (LEDs) which enabled efficient white light sources [35–37]. Deliberations in this section on the growth/synthesis techniques and properties of III-nitrides nanowires lay down a foundation to understand the III-nitrides optoelectronic devices which are discussed in subsequent sections.

2.1. Fabrication of III-nitride nanowires

Growth/synthesis techniques to realize III-nitrides nanowires can be categorized by mainly two approaches, namely: (i) top-down and (ii) Bottom-up process. A typical top-down method involves formation of nanoscale pattern and a subsequent etching process [38–42]. But inevitably top-down method brings major surface defects and damages in synthesized nanowires. Therefore, to reduce or cure these defects and damages post-etching annealing and/or wet chemical treatment has been regularly utilized [39,42–48]. A typical top-down method is presented in Fig. 1(a). A FE-SEM image of GaN nanowires which were realized in author's group by top-down method is shown in Fig. 2(a). However, to offer better control over growth parameters and sizes of nanowires, currently a large amount of research works is focused towards the bottom-up approach. A schematic representation of the bottom-up approach is shown in Fig. 1(b). The possibility of achieving radial or axial devices by depositing an active layer of optoelectronic devices on the nanowire sidewalls or along the growth direction during bottom-up method has attracted many researchers to employ this technique to realize nanowires. Many different growth techniques, namely: chemical vapor deposition (CVD), metalorganic chemical vapor deposition (MOCVD) or also identified as metalorganic vapor phase epitaxy (MOVPE), molecular beam epitaxy (MBE), and chemical beam epitaxy (CBE) have been established within the bottom-up category. Though the differences between these techniques are quite stark, the basic mechanisms in general can be categorized by (i) vapor-liquid-solid (VLS) and (ii) diffusion-driven growth process.

In 1964 Wagner and Ellis described the VLS growth technique for the first time while growing Si whiskers with Au catalysts [49]. A typical VLS growth process involves adatom adsorption, diffusion and precipitation. III-nitride nanowires growth via VLS technique has been studied extensively [50–60]. CVD/MOCVD techniques come in this class. Usage of different substrates likely sapphire, Si, GaAs and GaP also has been investigated. But involvement of foreign metal catalysts during the growth process induces stacking faults and deep trap states which results into reduced minority carrier lifetime and optical quality [58,61]. Fig. 2(b) shows a GaN nanowire array grown by VLS technique [62]. To overcome this challenge researchers have investigated the possibilities of developing

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