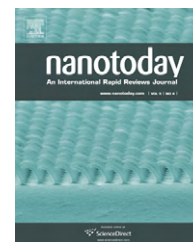




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REVIEW

One-dimensional II–VI nanostructures: Synthesis, properties and optoelectronic applications

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Summary The distinct properties of II–VI nanostructures have opened new opportunities for the applications of II–VI semiconductor materials in electronics and optoelectronics. Herein, we present a comprehensive review on the recent advances in the synthesis, properties and optoelectronic applications of one-dimensional II–VI nanostructures. In particular, the approaches to manipulate the electronic, optoelectronic, and transport properties of II–VI nanostructures by controlled doping and the latest progresses in fabricating high-performance II–VI nanoelectronic and nano-optoelectronic devices are discussed.

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Introduction

Discovery of carbon nanotubes (CNTs) in the early 1990s [1] has inspired a great interest in exploiting the promising potentials of one-dimensional (1D) semiconductor nanostructures in new electronic and optoelectronic device applications based on their specific geometries and distinct properties. Enormous efforts have been made to synthesize and characterize 1D nanostructures in the past two decades; and a host of nanostructures such as group IV, groups III–VI, groups II–VI, and oxide–semiconductor nanowires (NWs), nanoribbons (NRs)/nanobelts, and nanotubes (NTs), etc. have been successfully achieved. Among these nanostructures, 1D II–VI semiconductor nanostructures have shown

to be an important group with considerable progresses in the synthesis and utilization of their unique properties in extensive and novel applications [2].

We will start with a brief historical retrospect to the developments of II–VI materials, which may offer a conceptual understanding to the question why II–VI nanostructures have attracted such broad research interests. Wide band-gap II–VI semiconductors have been intensively studied for many years due to their great potentials for a variety of applications, in particular in the areas of electronic devices, phosphor, light-emitting and light-detecting devices, photovoltaic conversion (solar cells), X-ray and γ -ray detection, etc. [3]. Nevertheless, the industrial application of II–VI compounds is still at its infancy, and a part of the problems is associated with the synthesis techniques and the lack of understanding and control over the properties of II–VI compounds. For instance, CdTe has a band-gap of 1.5 eV which was suggested to be the optimum band-gap for photovoltaic solar energy conversion [4]. The direct band-gap of CdTe also

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leads to a high optical absorption coefficient for photons in the whole solar energy spectrum ($\alpha > 10^5 \text{ cm}^{-1}$), enabling the absorption of the most incident light in a relative thin CdTe layer of a few microns thick. As a result, the materials costs could be minimized and the requirement on the purity and crystallinity of CdTe films is not so strict due to the reduced diffusion length of photo-generated carriers. CdTe is a very promising material for high-efficiency thin film solar cells; and an efficiency up to 16.5%, against a theoretical maximum of 30%, has been indeed achieved on CdTe-based solar cells in labs [5,6]. In comparison, silicon has an indirect energy band-gap of $\sim 1.12 \text{ eV}$ and a low absorption coefficient of $\alpha \approx 100 \text{ cm}^{-1}$. A thick silicon layer of several hundred microns ($\gg 1/\alpha$) is needed, and the electron-hole pairs generated have to diffuse up to that distance to reach the electric field in the depletion region to contribute to the photocurrent [7]. Based on above, CdTe is expected to be a superior material to silicon in photovoltaic applications. However, the relatively poor reproducibility and uniformity of CdTe films over large areas result in a large difference between lab efficiencies of $\sim 16.5\%$ and the best module efficiencies of $\sim 10.7\%$ for CdTe solar cells [5], which hinders the scale-up market of CdTe-based solar cells.

II–VI compounds are also promising materials for optoelectronic applications, in particular for fabricating short-wavelength light-emitting diodes (LEDs) and laser diodes (LDs). Based on the achievement of p-type conduction via plasma-activated nitrogen doping, the first blue-green LD was developed from ZnSe in 1991 [8], which was about five years earlier than the report of the first GaN-based blue LD in 1996 [9]. The ZnSe LDs emitted coherent light at a wavelength of 490 nm, but it could work only at low temperature of 77 K with a short lifetime. Extensive efforts have been made to improve the output power and device lifetime of LDs. ZnCdSe continuous-wave (cw) LDs with a lifetime of about 100 h and LEDs with a lifetime up to 400 h under high current injection were achieved [10], and the use of ZnSe lasers in high-density CD players was also demonstrated [11]. However, some inherent problems such as poor electronic properties, low thermal conductivity, poor thermal stability, large Ohmic contact resistances, and low damage threshold have restricted ZnSe-based lasers to short lifetimes [12]. On the other hand, III-nitride industry has undergone an explosive development in the past decade since the demonstration of the first commercial blue GaN laser operating at 405 nm in 1998, which also resulted in a near halt to the then promising laser technology based on II–VI materials.

Owing to their high sensitivity and high quantum efficiency, II–VI photodetectors are ideally suited for light detection ranging from near infrared to ultraviolet, however II–VI photodetectors have thus far limited applications in some simple devices such as photoswitches in street lamps and photoresistors in some cameras. The most common detectors in the visible range are still fabricated from silicon even though Si suffers from the obvious disadvantages such as indirect band-gap in the infrared range. In addition to the visible light detecting, II–VI compounds, e.g., CdTe and ZnTe, have shown more attractive potentials in nuclear radiation detection at room temperature [13]; and the ternary CdZnTe compound also possesses favorable properties for X-ray and γ -ray detection, such as high atomic number (Z)

for efficient radiation–atomic interactions, high resistivity and low leakage current due to high purity and large band-gap, and high intrinsic $\mu\tau$ (μ is the carrier mobility, τ is the carrier lifetime) for efficient charge collection. These characteristics make CdZnTe an excellent candidate among a number of materials for high-energy radiation detection and high-performance spectrometers have been developed [14].

There are still more examples to illustrate the potentials of II–VI semiconductors in a variety of important applications. Nevertheless, difficulties in obtaining high-quality and homogeneous II–VI semiconductor films/bulks with high reproducibility, stability, and reliability pose serious obstacles to their practical utilization. Electronic and optoelectronic applications require still higher quality II–VI semiconductors with controlled defects and impurities. Therefore, the obtainment of device-quality and single-crystal II–VI semiconductor bulks/films is essential.

The advances in nanoscience and nanotechnology open new opportunity for the application of II–VI semiconductor materials. Because the requirement on the substrates for growth of high-quality, single-crystalline 1D nanostructures is not as strict as for epitaxial thin film growth, nanomaterials with high crystalline perfection, reduced defects and controlled doping are easier to fabricate. The crystal quality of the 1D nanostructures can be significantly improved compared to their thin film/bulk counterparts. In addition, the 1D semiconductor nanostructures exhibit distinct electronic and optical properties arising from unique geometries and size-confinement effects [15]. For example, single-crystalline wide band-gap 1D semiconductors can serve as nanoscale lasers, where the high refractive index contrast between the nanostructure and the surroundings defines a sub-wavelength-sized optical cavity [16,17]. They are also expected to function as waveguides for guiding and manipulating light on the sub-wavelength scale. The 1D nanostructures facilitate device fabrication since their length is usually in the range of micrometers, enabling processing and manipulation with the conventional technologies such as photolithography. The 1D system provides a fresh domain for basic physical studies as well as a new material system for next-generation electronic and optoelectronic devices [18].

Thus far, research related to II–VI nanomaterials has made great progress, ranging from synthesis of various nanostructures via different growth methods to applications in different fields. Since it is beyond the scope of this brief report to summarize all those previous works, we will restrict ourselves to first address the growth and doping of 1D II–VI nanomaterials, and then the recent advances in their electronic and optoelectronic applications. A comprehensive literature survey and bibliography are also included. On the other hand, we note that the oxide II–VI nanomaterials such as ZnO have already been extensively studied and reviewed [19]. Therefore, this review will be focused on the non-oxide II–VI nanomaterials instead.

Growth and doping of II–VI nanostructures

General approaches to grow II–VI nanostructures

The II–VI 1D semiconductor nanostructures are mostly synthesized by chemical vapor deposition (CVD), wet-

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