

Review Article

Diverse Role of Silicon Carbide in the Domain of Nanomaterials

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Silicon carbide (SiC) is a promising material due to its unique property to adopt different crystalline polytypes which monitor the band gap and the electronic and optical properties. Despite being an indirect band gap semiconductor, SiC is used in several high-performance electronic and optical devices. SiC has been long recognized as one of the best biocompatible materials, especially in cardiovascular and blood-contacting implants and biomedical devices. In this paper, diverse role of SiC in its nanostructured form has been discussed. It is felt that further experimental and theoretical work would help to better understanding of the various properties of these nanostructures in order to realize their full potentials.

1. Introduction

In present times group IV semiconductors, in general, are not as popular as they were before in the field of optics and optoelectronics. The reason lies in their indirect bandgaps, which make their luminescence efficiency very low at room temperature. In optoelectronics, devices made of group III/V composites such as GaAs dominate at the present time.

1.1. Superiority of Silicon Carbide over Silicon and Carbon.

Carbon is the backbone of all known life forms on earth. In the human body, it is the second most abundant element by mass after oxygen. Carbon in nature exists mostly in the form of graphite, diamond, and amorphous carbon. Silicon is the basic material used in integrated circuits and the principal component of semiconductor devices. Silicon is also an essential element to sustain life. The compound of silicon and carbon, silicon carbide (SiC), a semiconductor with superior characteristics, is widely used in high-temperature, high-power, and high-frequency electronic applications. It is also one of the best biocompatible materials.

1.2. *What Is So Fascinating about Silicon Carbide?* Bulk silicon carbide is a wide band gap IV-IV semiconductor with interesting and well-known physical properties. The band

gap of Si at room temperature is 1.12 eV whereas diverse for SiC because it exists in over 200 crystalline forms and among them the most common types are 3C, 6H, and 4H, which have band gaps of 2.2, 3.02, and 3.20 eV, respectively [1]. Silicon carbide is a promising material due to its unique ability to adopt different crystalline polytypes which monitor the band gap and then the electronic and optical properties [2–4]. Despite being an indirect band gap semiconductor, SiC is used in several high-performance electronic and optical devices due to its unique physical and electronic properties. High chemical stability facilitates SiC applications in hostile environments. Also, Silicon carbide has been long recognized as one of the best biocompatible materials [5], especially in cardiovascular and blood-contacting implants and biomedical devices.

1.3. *Suitability of SiC in Fluorescence: An Important Tool in Biological Research.*

Fluorescence is a detection method used in all aspects of biological research: bioanalytical assays, cell imaging, biosensors, and in vivo cell targeting. Thus, advances in biology and medicine strongly depend on the performances of fluorescence measurements. In particular, for cell imaging, efficient fluorescent nanoprobe are needed to detect very weak concentration of cancer cells in order to make early diagnoses. Combined to high-fluorescence

properties, an efficient nanoprobe must also be photostable, monochromatic, and weakly toxic. Semiconducting nanoparticles based on SiC were recently used successfully for the fluorescent imaging of living cells [6]. Known for its chemical and thermal stability, SiC is suitable for this application.

1.4. Quantum Dots: More Advantageous Substitute for Organic Fluorophores. Interest in semiconducting nanocrystals, or quantum dots (QDs), is growing because of their unusual physical properties, reported for particles that are less than few nanometers in diameter [7]. Photoluminescent QDs are increasingly being used as biological tags and are becoming an alternative to traditional organic dye based fluorophores [8]. Their main advantages over organic fluorophores are superior stability against photobleaching and size-tunable emission wavelength.

1.5. Reason Why Group IV Nanostructures Dominate in Modern Era. With the advent of nanoscience and nanotechnology, there has been increasing interest in obtaining efficient luminescence from group IV nanostructures for two reasons. First of all, extensive investigations have demonstrated that the fluorescence efficiency in group IV nanostructures can be improved by several orders of magnitude with respect to that of bulk materials. Their quantum yield can be closer to or even higher than those of some bulk or nanostructured direct band gap semiconductors. This results from substantially enhanced radiative recombination rates and suppressed or relatively reduced nonradiative recombination rates due to spatial confinement in the nanostructures [9]. Secondly, group IV nanoparticles are more benign to human beings and environments compared with semiconductor nanocrystals that contain cytotoxic heavy metal atoms. Thirdly, fluorescent semiconductor (including group IV) nanocrystals, also known as quantum dots, have demonstrated their great potential in biological imaging and diagnostics as they have such virtues superior to traditional organic dyes as high resistance against photobleaching, composition/size-dependent absorption, and emission, as well as broad absorption spectra and narrow emission spectra (for monodisperse nanoparticles) [10, 11]. Hence, they are suitable for long-term and multicolor labeling in the monitoring of intracellular processes [12–14]. Furthermore, they can serve as drug delivery platforms in therapeutics. In this respect, group IV nanoparticles bring new hopes as benign materials accompanied by the above-mentioned properties, which favor their biological applications.

Another advantage of group IV nanostructures is that they can be readily made water-soluble as-prepared or via subsequent surface functionalization; this is a necessary condition for applications in a physiological environment. Also, all the group IV materials can form chemical bonds with various types of ligands especially biomolecules [15].

According to the quantum confinement effect, as the size of a semiconductor particle diminishes to be near or smaller than its bulk exciton Bohr diameter, the corresponding energy gap will increase with decreasing size, and accordingly

its fluorescence arising from interband transitions of carriers (electrons and holes) will shift to blue [16]. As a result, the emissions in group IV nanoparticles with different sizes will span the whole spectral region from near-IR to visible to near-UV. This virtue is favourable for their applications in biological imaging and sensing.

1.6. Silicon Carbide Nanostructures versus Silicon Nanomaterials. The physical properties of functional hybrid nanocomposites were intensively investigated during the last decade. Among the reported functionalities, those in optics [17], electronics [18], photovoltaic [19], or optoelectronics [20] are very promising. As far as the functionalities are concerned, the active vectors consist in inorganic semiconducting nanocrystals.

Silicon nanoparticles, despite being comprised of an indirect band gap material, can exhibit photoluminescence at visible wavelengths, an effect attributed to quantum confinement [21]. Unlike their direct band gap counterparts, silicon nanomaterials are bioinert [22] but their wider acceptance as alternative fluorophores is presently limited by poor emission stability in aqueous environments [23]. Nanostructured silicon carbide has unique properties that make it useful in microelectronics, optoelectronics, and biomedical engineering and have thus attracted much interest from the materials and device communities. In the microelectronics industry, silicon carbide is regarded as a promising substitute for silicon, especially in high-power, high-temperature, and high-frequency devices [24, 25]. This wide bandgap biocompatible [26] material was recently shown to exhibit blue/yellow photoluminescence in nanoscale structures [27]. The SiC nanoparticles are characterized by versatile properties such as dielectric behavior marked by interfacial polarizations [28–30] as well as the vibrational and luminescence properties which point out the main role of surface nature [3, 4].

The luminescent properties of SiC nanocrystals have been observed to be quite variable and strongly depend on the fabrication methods and even on the specific measurements. The emission band can span a wide spectral range from 400 to 500 nm. No luminescence exhibiting obvious quantum confinement has been reported until recently. This is in contrast to porous Si [21, 31] and Si nanocrystals [32–35] from which quantum confinement can be more easily observed. As a binary compound, silicon carbide has complex surface states and structures [36–39]. The main reasons why quantum confinement is not easily achieved in SiC are that there are many surface or defect states which dominate the luminescence and that the SiC nanocrystals are too large [40].

On the theoretical front, the results of investigations on the structure and electronic properties of SiC nanostructures, employing semiempirical and first-principle calculations [41–43] suggest that the band gap of SiC nanostructures has a strong dependence on their sizes and surface compositions.

1.7. Charisma of Different Varieties of SiC Nanostructures. Among the different kinds of SiC nanostructures, SiC nanocrystals which have potential applications as nanoscale

light emitters were the first to receive attention and have been studied extensively in the last fifteen years. Optically, bulk SiC shows weak emission at room temperature on account of its indirect band gap [44]. However, the emission intensity can be significantly enhanced when the crystallite size diminishes to several or tens of nanometers [21, 45]. This is thought to be caused by depressed nonradiative recombination in the confined clusters [33]. In accordance with the quantum confinement (QC) effect, photoluminescence (PL) of the crystallites with diameters below the Bohr radius of bulk excitons is shifted to blue with decreasing sizes [46, 47]. Consequently, wavelength-tunable emissions can be achieved by preparing crystallites with different sizes. The large band gap of SiC (2.23 eV for 3C-SiC) renders the nanocrystals a good candidate as blue and ultraviolet (UV) light emitters in displays. This is in contrast to silicon crystallites from which strong and stable emissions in these spectral ranges are difficult to achieve [45]. Moreover, the high chemical and thermal stabilities [48] of silicon carbide make the luminescence from these nanocrystals very stable enabling the use of the materials in harsh environments and demanding applications. Combined with their excellent biocompatibility, especially blood compatibility, low density, and high rigidity [1, 49], SiC nanocrystals are potentially useful in biology and medicine as well, for example, in biolabelling [7, 50].

Recently, one-dimensional (1D) SiC nanostructures such as nanowires [51] and nanotubes [52] have attracted a lot of interests because they play a crucial role as the building blocks in molecular electronics [53]. Silicon carbide nanowires that have outstanding mechanical property and high electrical conductance can be used to reinforce composite materials or as nanocontacts in a harsh environment. Moreover, the materials have good field electron emission properties and biocompatibility.

The optical and electrical properties of nanometer-sized silicon carbide structures are particularly crucial to efficient and stable SiC nanodevices. SiC nanowires have been shown to have stable field electron emission properties [54, 55], suggesting that the materials have potential as field electron emitters. The heterostructures of single-walled carbon nanotubes and silicon carbide nanorods [56] may play an important role in future hybrid nanodevices. The intense, robust, and wavelength-tuneable visible emission from 3C-SiC nanocrystals shows that they are good light sources [27] applicable to nanooptoelectronic integration. Nanocrystalline SiC films which emit visible light [57] are also promising in large area displays. Furthermore, silicon carbide is a biocompatible material [58] and biosensors made of these materials may be realized in the future. Considering the chemical stability and water-solubility, luminescent silicon carbide nanocrystals may find applications in biotechnology/medicine [59].

Bulk silicon carbide is a wide band gap IV-IV semiconductor with interesting and well-known physical properties. Nanoscale engineering of this material allows considerable extension of its basic physicochemical properties. For example, SiC nanostructures have shown greater elasticity and strength than bulk SiC [60], and SiC nanowires have an

electron field emission threshold comparable to that of a carbon nanotube-based material as well as stable emission properties [55]. Niu and wang [61] recently reported an application of SiC nanowires covered with platinum as an efficient electrocatalyst for hydrogen adsorption/desorption and methanol oxidation. Various SiC nanostructures such as nanospheres, nanowires, nanorods, nanopowders, and even nanoflowers have been developed [51, 56, 62–66]. Special efforts of the researchers were oriented to grow SiC nanoparticles on Si substrates [67, 68]. Incorporation of SiC nanostructures into polymer matrices to form new kinds of composite materials was also carried out and studied [69]. For example, a linear electro-optic effect in polymer matrices containing SiC nanocrystallites was experimentally observed and reported [70].

2. Mechanical Alloying: A Superior Fabrication Technique

Usually, metal carbides are prepared by conventional powder metallurgy route, liquid phase sintering technique [71, 72], solid vapor reaction process [73], or chemical vapor reaction [74] which requires a very high temperature as well as good vacuum condition or ultra-pure inert gas atmosphere. One “top down” physical method for preparing homogeneous nanocrystalline metal carbides is mechanical alloying (MA) [75–85]. MA has the advantages over other fabrications techniques as the final product takes a nanocrystalline structure with superior properties in comparison to conventional coarse grained materials. Enayati et al. and Abderrazak and Abdellaoui reported that nanocrystalline SiC can be prepared using MA [79, 85] with a very high ball-to-powder mass ratio (BPMR \sim 67:1). Amorphisation of Si during mechano-synthesis of SiC has been reported by several authors [86, 87].

2.1. Phenomena Associated with Mechanical Alloying. Heavy plastic deformation such as MA introduces a high density of lattice imperfections in prepared materials, which are responsible for the observed peak broadening of their X-ray diffraction powder pattern [88, 89]. Besides peak broadening, peaks may also become asymmetrical and/or shift with respect to their unmilled counterpart due to plastic deformation. All these effects on diffraction profile of a ball-milled sample (cold-worked) are related to several microstructural parameters like: change in lattice parameter, residual stress, density of stacking, twin/growth faults, coherently diffracting domain size (particle size), r.m.s. lattice strain, dislocation density, and stacking fault energy.

2.2. Preparing Tailor-Made Nanocrystals. All the microstructural parameters can be estimated quantitatively by analyzing the XRD patterns of ball-milled samples employing Rietveld's structure refinement method. The Rietveld's method of analysis based on structural and microstructural refinement is the best approach to characterize microstructure of ball-milled samples containing lattice imperfections of different kind. As the microstructural parameters are directly related to several physical properties of a material,

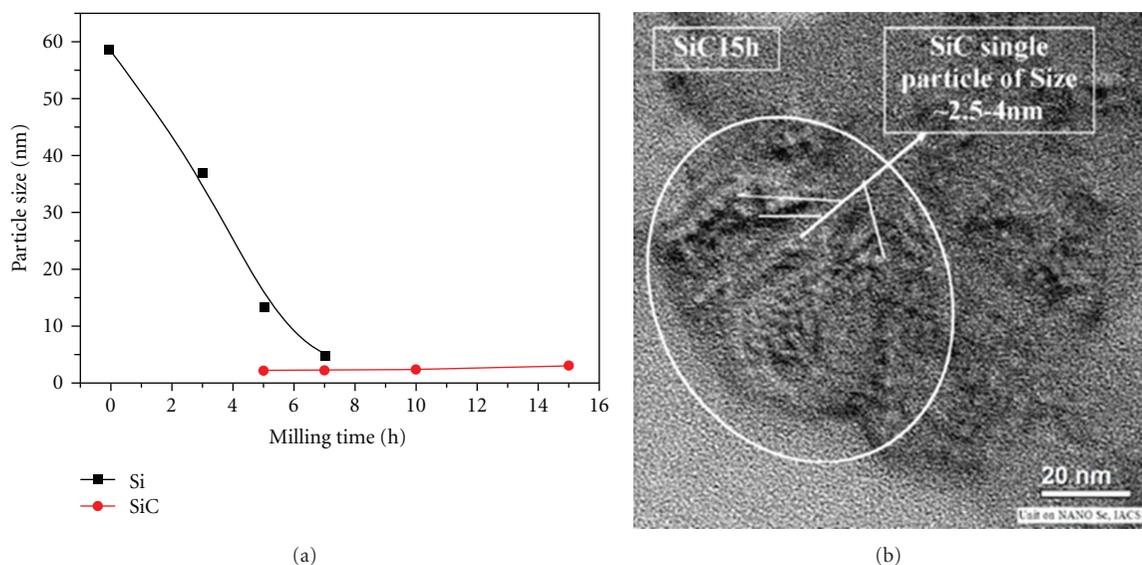


FIGURE 1: (a) Particle size of Si and SiC phases in unmilled and ball-milled mixture of Si and graphite (1 : 1 mol) with increasing milling time. (b) HRTEM micrograph of SiC phase after 15 h ball-milling.

a control over the microstructure leads one to prepare “tailor made” materials having desirable properties.

Ghosh and Pradhan [90] mechanically alloyed the elemental Si and C (Graphite) powders under Ar using a high-energy planetary ball mill at room temperature for different durations and then investigated the alloying mechanism during MA by successive modifications of X-ray powder diffraction pattern of ball-milled samples. The microstructural characterisation of ball-milled samples, done by the authors, by Rietveld’s analysis, reveals that at the early stage of milling, graphite layers are distributed on the Si nanograin boundaries as very thin layers and full formation of nanocrystalline SiC phase is observed after 15 h of milling (Figure 1).

3. Conclusion: Goal Is yet to Be Reached

As silicon-based microelectronic devices are approaching the physical limits, the constant push to develop better and faster devices and higher computing power has spurred the development of substituting materials. In this regard, silicon carbide is a good candidate in high-power, high-temperature, and high-frequency applications.

Extensive studies on silicon carbide nanostructures such as nanocrystals, nanowires and nanotubes, and nanosized films began in the mid-1990s, and we have aimed, in this paper, at reviewing the role of SiC nanostructures in the field of photo science, in a broad sense, already published in the past years. However, it should be noted that researches on silicon carbide nanostructures are still in the beginning stage. Contrary to nanostructured silicon, SiC nanostructures have been subjected to a much smaller amount of theoretical and experimental works devoted to the understanding of the light-induced electronic processes. Although clear quantum confinement of 3C-SiC has been observed [91], the specific defect or surface states responsible

for the observed luminescence have not been unequivocally identified. Much more experimental and theoretical work is needed. Finally, there have only been a few theoretical studies on SiC nanostructures. A better understanding of the various properties of these nanostructures is needed in order to realize their full potentials.

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