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S. Castelletto, B. C. Johnson, I. Aharonovich, A. Parker, "Fluorescent emission in different silicon carbide polytypes," Proc. SPIE 8923, Micro/Nano Materials, Devices, and Systems, 89230B (7 December 2013); doi: 10.1117/12.2033265

Event: SPIE Micro+Nano Materials, Devices, and Applications, 2013, Melbourne, Victoria, Australia

FLUORESCENT EMISSION IN DIFFERENT SILICON CARBIDE POLYTYPES

S. Castelletto[1*], B.C. Johnson[2,3], I. Aharonovich[4] and A. Parker[1]
[1] School of Aerospace, Mechanical & Manufacturing Engineering
RMIT University, Bundoora, VIC, Australia
[2] School of Physics, The University of Melbourne, VIC, Australia1
[3]CQC2T, University of Melbourne, Parkville, VIC 3010, Australia
[4]School of Physics and Advanced Materials, University of Technology Sydney, Ultimo, NSW 2007, Australia
[*]Corresponding author email: *stefania.castelletto@rmit.edu.au*

Abstract

Silicon carbide (SiC) is a widely used material in several industrial applications such as high power electronics, light emitting diodes, and in research application such as photo-voltaic and quantum technologies. As nanoparticles it can be synthetised in many sizes and different polytypes from 200 nm down to 1 nm. In the form of quantum dots they are used as optical biomarkers, and their emission, occurring from the blue to the orange spectral region, is based on quantum confinement effect. In this work we report on emission in the red and near infrared in different SiC polytypes, specifically in 4H, 6H and 3C. In 4H SiC the red visible emission yielded non classical light attributed to an intrinsic defect, identified as a carbon-antisite vacancy pair. Similar spectral emission was observed in 3C SiC bulk and nanoparticles, also yielding very bright single photon emission. Emission in the far red has been observed in homogeneous hetero-structure in SiC tetrapods.

Keywords: optical defects, silicon carbide nanoparticles, non-classical photo-emission, confocal microscopy

1. INTRODUCTION

SiC is a compound of silicon and carbon that exists in many different crystal types (well over 200 polytypes), and as a semiconductor with a wide-band gap (depending on the polytypes), it has an high thermal conductivity, the ability to sustain high electric fields before breakdown, and the highest maximum current density, making it ideal for high power electronics[1]. Such an engineer-friendly material used since many years, has also recently attracted attention in emerging research fields such as quantum computing[1–3], spintronics[4] and single photon generation[5], as several of its intrinsic defects carrying an electron spin can be used as "quantum bits" and more recently they have been isolated providing single photon emission at room temperature.

Its relevance and promises to provide a platform for quantum technology rely on SiC high quality and ultra-pure large scale production and ready available nanofabrication methods in a large variety of technologies.

At the nanoscale SiC nanoparticles possess several similarities with other semiconductors quantum dots. For a review on quantum properties in silicon carbide see ref [6].

This paper will review very recent research by the authors in bulk and nanostructures SiC, indicating that this material could result in an advanced platform for the integration of active single defect (quantum system) in existing device technologies (photonics, electronic devices and nano-mechanical resonators) with the exceptional possibility to operate at room temperature.

Among SiC many polytypes only three are of technologically importance because can be produced as high quality, bulk single crystal substrates and films. Two of these polytypes have an hexagonally arranged bilayer configuration with a 4 and 6 bilayer periodicity, referred to as 4H-SiC and 6H-SiC, respectively. The structure of the third polytype is cubic of the zinc-blende type and is referred to as 3C-SiC. The 4H and 6H-SiC polytypes can be readily produced in electronic-grade wafers suitable for epitaxial growth. Creating high quality 3C-SiC wafer-type substrates has been significantly more challenging, although, production of large-area 3C-SiC wafers has been demonstrated. Here we will show recent results on photoluminescence studies in 4H, 6H and 3C SiC.

Micro/Nano Materials, Devices, and Systems, edited by James Friend, H. Hoe Tan, Proc. of SPIE
Vol. 8923, 89230B · © 2013 SPIE · CCC code: 0277-786X/13/$18 · doi: 10.1117/12.2033265

2. **Bright single photon emission in ultra-pure 4H SiC**

A range of deep level defects give rise to radiative recombination in SiC. Defect-induced photoluminescence (PL) in SiC can be detected from the UV to the infrared with some PL lines coinciding with the first and second telecommunication windows. The binary compound nature and the existence of non-equivalent lattice sites in different polytypes gives rise to a large variety of possible defects. Combinations of simple point defects are possible, of recent interest di-vacancies $(V_{Si}V_C)$[3] and C vacancy-antisite pairs (V_CC_{Si})[5].

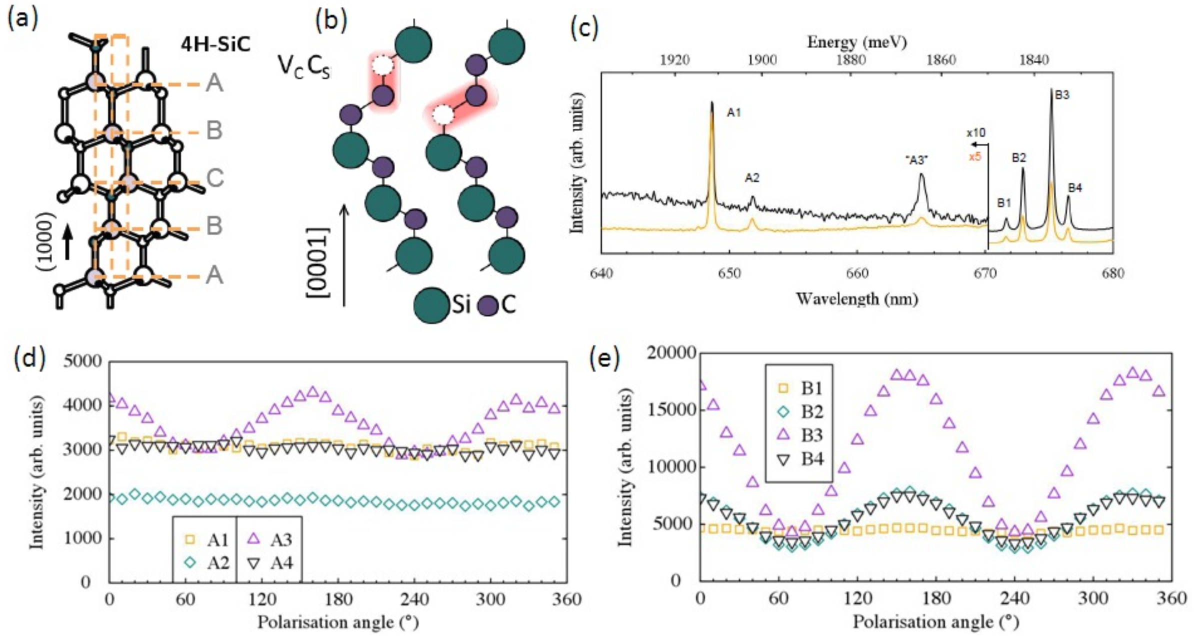

Figure 1 (a) 4H SiC atoms layout. (b)The proposed atomic structure of the defects $C_{Si}V_C$, giving rise to the photoluminescence, is shown in the (1000) plane (small and large circles represent C and Si atoms; the small open circles are vacancies).
(c)The AB photoluminescence lines observed in an electron-irradiated sample measured at 80 K. (d,e), The emission polarization dependence of the AB lines with the excitation beam perpendicular to the c axis.

Before the full use of these defects can be realized in applications relative to quantum technologies or quantum sensing, a number of challenges need to be addressed. Spin manipulation has so far been carried out only for ensembles of defects[3]. A first step towards the application of SiC defects in quantum technologies is to observe single photon emission from SiC defects. Such single photon sources have been observed for the first time operating at room temperature.[5] These particular defects are C anti-site-vacancy pairs, firstly identified in ensemble[7], giving rise to the AB PL system[8]. The single photon statistics for emission from a single C anti-site-vacancy pair and the defect creation in ultra-pure 4H SiC are described in ref [5]. In Figure 1 (a) 4H Silicon Carbide structure is shown together with the specific defect atomistic structure (b). This defect is the brightest single photon emitter in a solid state system operating at room temperature, indicating a quantum efficiency of about 70%. C anti-site-vacancy pair occurs in the region 650-700 nm due to the existence of eight Zero Phonon Lines (ZPLs) associated to different location of the defect in the lattice, known as axial and basal sites. PL emission of the various ZPLs is shown in Figure 1 (c) at low temperature for all AB lines, while Figure 1 (d) and (e) show the polarization of the A and B lines which is in agreement with the modelled symmetry of the defect[5]. At room temperature a single line results broadened.

4H SiC samples were carefully irradiated with electrons at high energy (2MeV) and various fluences (from 10^{13} to 10^{17} e/cm^2) to create vacancies and then annealed at various temperatures (from 300 to 800◦C). We performed confocal microscopy to identify bright spots on the confocal maps using 532nm and 660 nm excitation laser. We verified single photon emission using a Hanbury-Brown and Twiss interferometer and analysed the photo-luminescence (PL) at room temperature[5]. Ensemble PL measurements and PL polarization were performed at low temperature.

3. PL emission in 4H and 6H SiC devices

SiC pn junction diodes in both 4H and 6H polytypes have been fabricated[11]. The optically active defects in these devices are investigated using both photoluminescence (PL) and electroluminescence (EL) techniques.

Various p+n juncton diodes were formed with 4H and 6H SiC n-type epilayers grown by hot-wall chemical vapour deposition. Defects in the as-prepared devices and those introduced by implantation and electron irradiation are investigated. To characterise the defects a Renishaw MicroRaman Spectrometer was used for the Raman scattering, PL and EL measurements. A 532 nm laser was directed through a 20x long working distance objective with a 0.4 NA onto the sample. The visible wavelength range detector is a fan cooled Si CCD while the NIR detector is a LN2 cooled InGaAs photodiode array.

To understand the evolution of defects in SiC and to optimize their incorporation into SiC devices an annealing study was first performed on 4H SiC irradiated with 2 MeV electrons to a fluence of 1x10^{17} cm^{-2}. The annealing kinetics of the $C_{Si}V_C$ defect is compared with that of the (V_{Si}) and the divacancy (V_CV_{Si}). The V_{Si} defect which has ZPL emission around 861.5 and 916.3 nm is the most unstable and the PL decreases dramatically around 600^{o}C. The $C_{Si}V_C$ defect has eight ZPLs in the 648-675 nm range and increases in intensity until 800^{o}C after which it anneals out. The V_CV_{Si} defects with ZPLs in the NIR are the most stable and peaked in intensity at 1000^{o}C but were not annealed out in the annealing range considered.

Figure 2 shows the PL spectra of the as-prepared SiC devices. All devices showed Raman features and current voltage characteristics indicative of a high quality device. However, broad PL features were observed in the 700-1000 nm range. EL was also observed while the devices were under bias (not shown).

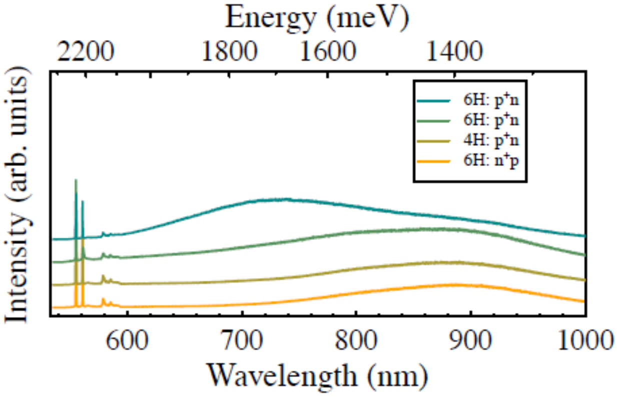

Figure 2- PL spectra of the 6H-SiC devices at room temperature.

3. 3C SiC nanoparticles

Semiconductor nanocrystals have enabled or transformed research in technologically important areas including bio-labelling, solid state lighting, and quantum information processing.

At the nanoscale, SiC shows quantum confinement effect and luminescence properties within the 400-460 nm emission range[9]. SiC nanoparticles can be produced in sizes as small as 1.4 nm and no protective shells are needed for making SiC QDs biocompatible or for stabilizing them in aqueous systems. The fabrication of colloidal SiC quantum dots has been achieved from milling different polytypes (3C, 6H, and 4H) of bulk SiC crystals using electrochemical method. The three types of obtained SiC QDs show quite-similar photoluminescence and photoluminescence excitation properties. The photoluminescence peak (in the visible from 450 nm to 600 nm) depends on the excitation wavelength and their lifetime is in the few ns region.

In this work using confocal microscopy and AFM combined with and Hanbury-Brown interferometer (Figure (d) and (e)), we studied SiC nanoparticle PL, observing a broad band emission at room temperature further in the red region with a peak around 700 nm in nanoparticles of about 250 nm size (Figure 3(b)). This emission resulted very bright and in a similar spectral region of the 4H single photon source defect, therefore it is likely to be attributed to the same defect. Further experimental and theoretical work is needed however to fully identify this defect in 3C[12]. Single photon emission has been observed (not shown) [12]. As a comparison PL were also studied in bulk n-type 3C SiC (Figure 3 c).

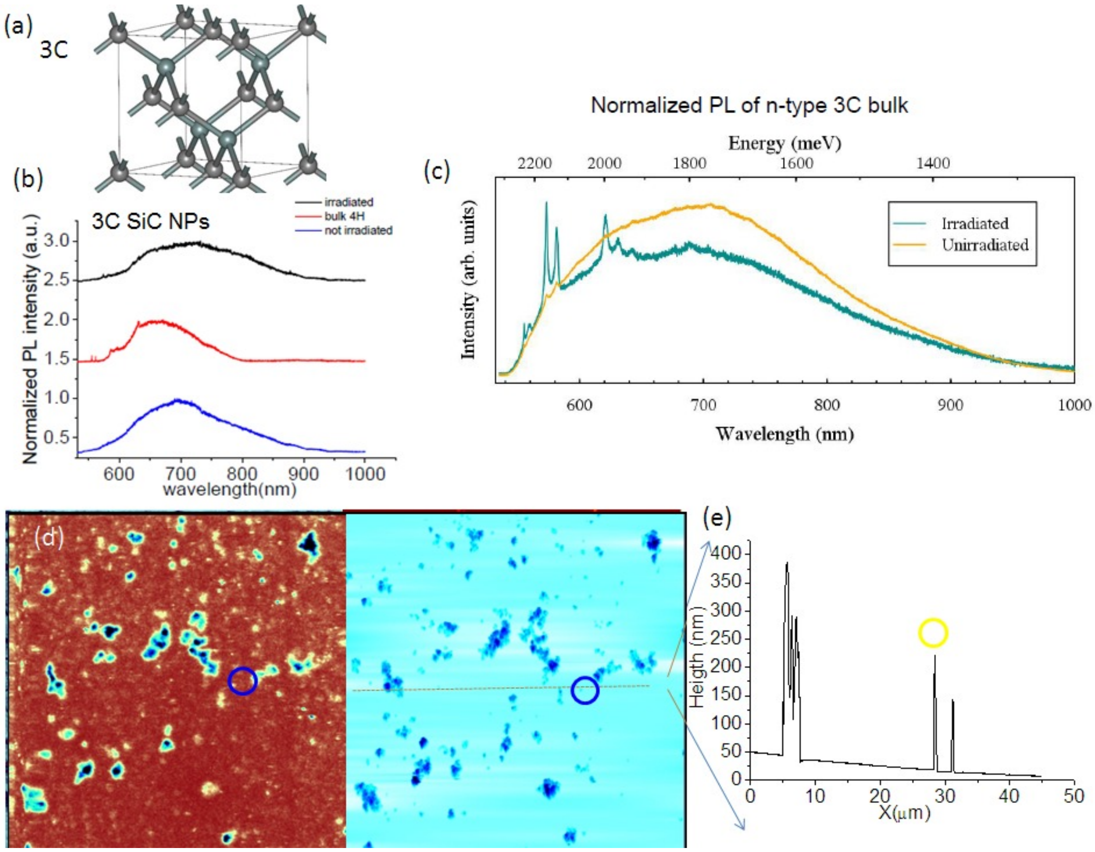

Figure 3- (a) Structure of 3C SiC from Wikimedia Commons. (b) Normalised PL from oxidised commercial 3C SiC nanoparticles from electron irradiated samples and not irradiated samples. A comparison with emission in bulk 4H, yielding single photon emission is shown. (c) Normalised PL from electron irradiated and not irradiated bulk n-type 3C SiC. (d) 45x45 μm^2 *confocal and AFM scan of the same area of spin coated 3C SiC nanoparticles (NP) on a cover glass. The circle corresponds to a non-irradiated nanoparticles with PL shown in (b) (e) Cross section providing the height of the SiC NPs studied from the AFM scan.*

1. SiC tetrapods

The emission properties of quantum dots can be controlled by adjusting their size, altering the material composition, or by building core–shell type structures to improve exciton confinement. Increased structural complexity of a nanostructure can yield even greater control over its excitonic and optical properties.

Another interesting nanostructures in SiC have recently been synthesized via microwave plasma enhanced chemical vapor deposition from seeding a silicon substrate using adamantane[10].Tetrapods grown by this technique have four legs, 3C SiC is nucleated from adamantane in the Si-rich sol gel environment while the growth environment was carbon-rich, promoting a transition to the growth of 4H-SiC. The coexistence of 3C and 4H in these nanostructures corresponds to homogeneous hetero-structure giving rise to PL in the spectral region between 600 nm and 800 nm. In this case the emission is consistent with spatially indirect exciton transition from the 3C core to the 4H legs, due to a narrower full width half-maximum emission (FHWM) of 5 nm at room temperature, which cannot be associated defect typically created in SiC[13].

Figure 4(a) shows scanning electron microscope image of the tetrapods. The tetrapods exhibit some variation in size and symmetry and do not exhibit a preferred growth orientation. The legs are 40 ± 10 nm in diameter and 90 ± 20 nm long. Through detailed investigation of the structural and compositional properties of the SiC tetrapods, it is determined that the tetrapods have 4H arms and likely grow from a 3C core.

Remarkably, the tetrapods exhibit narrow band fluorescence as shown in Figure 4(b). The emission maximum varies for different tetrapods, appearing between 550 and 800 nm and having a FWHM of ~5 nm – the narrowest emission known for any quantum dots or tetrapod structures. The variation in PL is believed to arise from structural differences among the different tetrapods.

Finally, detailed correlation measurements reveal the most of the tetrapods exhibit single photon emission, as confirmed by measuring the photon statistics of the emitted light (not shown). This makes the SiC tetrapods a prime candidate for future sensing and quantum applications[12].

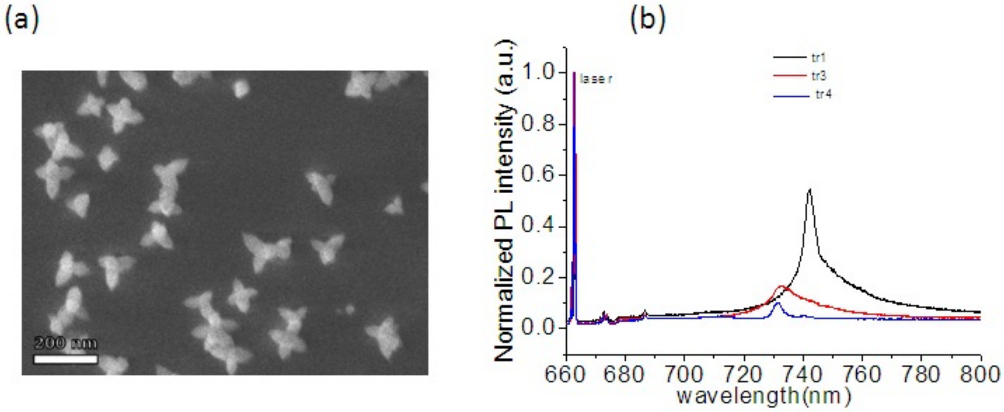

Figure 4. (a) SEM image of SiC tetrapods (b) PL measured on single tetrapods identified using confocal microscopy.

2. SUMMARY

Red and near infrared photoluminescence in various polytype of SiC such as 4H, 6H and 3C are presented. As striking novelty if compared to the present literature on PL in SiC, under confocal microscopy with single defect sensitivity, we observed a strong PL in all polytypes in the region from 600 nm to 700 nm, in some cases yielding single photon emission[5]. This PL can be present in as grown material and enhanced in electron irradiated materials. In 4H SiC this emission has been attributed to a defect identified as carbon–antisite vacancy pair as the modelling of this defect agrees with the experimental observation for what concerns its PL polarization properties. Similar broad band emission is observed in 3C nanoparticles and 3C bulk material, with the expected enhanced emission occurring in 200 nm nanoparticles size. In this polytype the appurtenance of the defect is still debated. Finally emission in the far red and near infrared (600 to 800 nm) with narrower FWHM at room temperature is observed from SiC tetrapods. Due to the heterostructure of the tetrapods, made of 3C and 4H SiC with nanoscale sizes, this PL is motivated by exciton quantum confinement.

Presently SiC is the most prominent and rich material system being investigated from the point of view of optical deep defects as well as quantum confinement avenues, due to different polytype engineering of nanostrucutres. Intrinsic relevant defects can be created in the material from the single to the ensemble level with electron irradiation.

SiC nanoparticles also harbour stable intrinsic defects with single photon emitter, therefore we believe that this will be a rich platform for future investigation towards technological advanced systems and novel physics to be discovered.

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