

## 3C-SiC AS A FUTURE PHOTOVOLTAIC MATERIAL

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### ABSTRACT

Cubic silicon carbide (3C-SiC) is being investigated for two Third Generation photovoltaic (PV) devices – the impurity photovoltaic (IPV) solar cell, and a silicon carbide/silicon superlattice structure for the upper cell in a tandem solar cell.

### 1. INTRODUCTION

As silicon solar cells slowly approach their theoretical efficiency limits, alternative materials and photovoltaic (PV) device structures are being investigated. The primary aim is to develop a solar cell that can overcome two loss mechanisms – lattice thermalisation of generated carriers that have an energy much greater than the bandgap ( $E_g$ ) of the semiconductor, and for sub-bandgap photons that are not absorbed.

Beta ( $\beta$ ) or cubic silicon carbide (3C-SiC) is being investigated for two Third Generation photovoltaic devices. The reasons for investigating 3C-SiC as a future semiconducting material for the PV industry include:

- i) both carbon and silicon are abundant and non-toxic;
- ii) as with silicon-based technology, silicon dioxide ( $\text{SiO}_2$ ) passivation layers can be thermally-grown to passivate 3C-SiC;
- iii) a large SiC power-electronics market is currently under development, and advances in this area could be capitalised upon by PV;
- iv) 3C-SiC exhibits excellent electronic properties including high electron mobility and saturated electron drift velocity;
- v) single-crystal 3C-SiC wafers are expected to be commercially available in mid-2003 [2], and epitaxial layers of 3C-SiC can be grown on silicon (c-Si) wafers using atmospheric pressure chemical vapour deposition (APCVD) [3];
- vi) 3C-SiC exhibits the lowest  $E_g$  (2.2 eV) of all SiC polytypes, and shows promise as a material for several multiple-threshold device structures [1,4].

Many challenges remain to be overcome however, before an efficient solar cell can be fabricated on any SiC polytype. 3C-SiC exhibits a lower refractive index than silicon ( $n \sim 2.6$ ), reducing the effectiveness of light trapping while the lack of a shallow  $p$ -type dopant limits the flexibility in device design [4].

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Due to the outstanding stability of 3C-SiC, standard PV processing techniques such as thermal diffusion would need to be performed at temperatures  $>2000^\circ\text{C}$  [5]. However, alternative techniques for junction formation could include changing gases during CVD film growth, or high temperature ion-implantation [5].

PV devices have already been fabricated from both hexagonal silicon carbide (6H-SiC) and amorphous silicon carbide (a-SiC). 6H-SiC solar cells were chosen for use in space due to the excellent radiation hardness exhibited by all forms of SiC [6], while a-SiC layers are commonly used as a  $p$ -type emitter layer in amorphous silicon (a-Si) tandem solar cells due to its high bandgap [7].

### 2. THIRD GENERATION PHOTOVOLTAIC DEVICES

The tandem solar cell is probably the most common device that fits into the Third Generation category, and is able to respond to different wavelengths of light by using a stack of vertically integrated solar cells fabricated from materials with a decreasing bandgap. An example of this is shown in Figure 1, for a 3C-SiC upper cell and a Si lower cell [1].

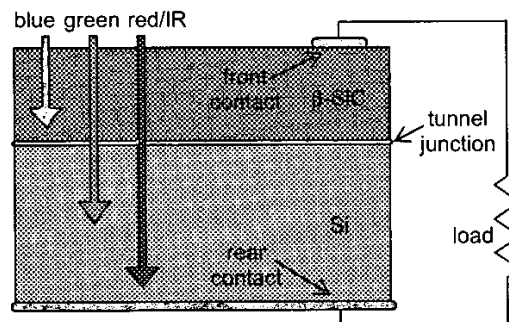


Fig. 1 3C-SiC/Si tandem solar cell [1].

An initial study revealed that while the bandgap of 3C-SiC is the lowest of all SiC polytypes, it is still too high to act as an optimal upper cell in a tandem structure based on a lower silicon solar cell, and that the ideal bandgap lies in the 1.6 – 1.8 eV range. This is demonstrated graphically in Figure 2, where the performance of the  $\beta$ -SiC/Si tandem cell is, at best, only equal to that of the Si single-junction cell under AM1 [1].

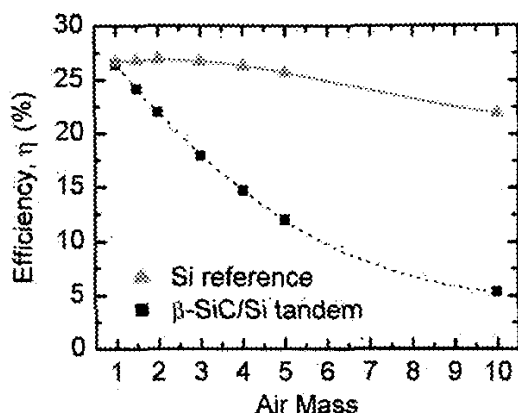


Fig. 2 The performance of a 3C-SiC/Si tandem solar cell (■) is poorer than a single-junction Si cell (△) under all air-masses [1].

Therefore a superlattice structure has been proposed, composed of alternating nanometre thick layers of 3C-SiC and c-Si. In this manner, a new material could be created with the desired effective bandgap using only group IV elements. The traditional disadvantage of tandem solar cells, that of current mismatch, however, cannot be avoided in a standard two-terminal connection (such as that shown in Figure 1).

Boron-doped cubic silicon carbide (3C-SiC:B) has been suggested as one possible candidate for the fabrication of an impurity photovoltaic (IPV) solar cell. The previously mentioned tandem solar cell, relies on sub-bandgap light of top (high  $E_g$ ) cell being absorbed and collected in the bottom (low  $E_g$ ) cell and can be considered as two separate devices. However, the IPV device is based on a wide bandgap semiconductor, but includes an intermediary defect or trap level that is designed to assist the absorption of sub-bandgap light [6]. Theoretical predictions have indicated that a conversion efficiency of  $\eta = 48.9\%$  can be achieved with a single defect level [8]. Furthermore, the ideal bandgap has been shown to lie in the range 2.0 – 2.5 eV, with a defect level  $E_T$  lying one-third of the distance (0.6 – 0.8 eV) above the valence band  $E_v$  or below the conduction band  $E_c$  [4].

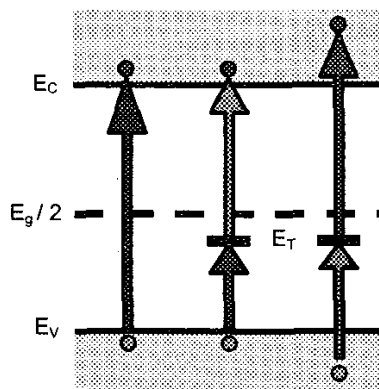


Fig. 3 Absorption of sub-bandgap light possible in IPV device via trap level  $E_T$ , as well as band-to-band absorption.

As shown in Figure 3, this allows electron hole (e-h) pair generation to occur via band-to-band transitions, as well as radiative transitions that occur via the trap level. Naturally, the latter transitions much also compete with simultaneously occurring recombination events, and the overall generation will depend on the relevant generation and recombination rate.

### 3. 3C-SiC/Si SUPERLATTICES

In an effort to fabricate 3C-SiC/Si superlattices, alternating layers of amorphous silicon carbide (a-SiC) and amorphous silicon (a-Si) have been deposited onto Si wafers and quartz substrates. In the past, many silicon superlattice structures have been investigated, including  $\text{SiO}_2/\text{Si}$  [9] and a-SiC/a-Si [7,10], however no work has been reported to date on crystalline 3C-SiC/Si superlattices to our knowledge. Figure 4 shows a transmission electron microscopy (TEM) image of a 10 bilayer a-SiC/a-Si superlattice structure, deposited using plasma enhanced chemical vapour deposition (PECVD). The layers are about 4 nm thick, a and the methane and silane gas flows were adjusted to obtain a-SiC films with a Si:C ratio of about 1:1. A secondary ion mass spectroscopy (SIMS) of the a-SiC/a-Si sample is provided in Figure 5, and ten peaks can be resolved. The resolution of the SIMS data is 5 nm and the layer thickness 3 – 4 nm, which explains why the carbon signal does not decrease to zero in the a-Si layers, as may otherwise be expected.

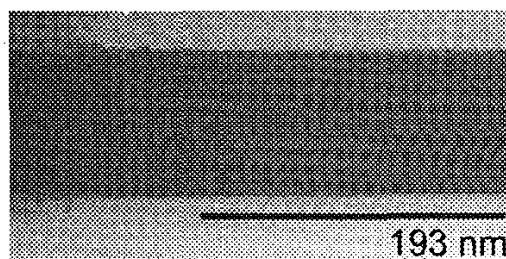


Fig. 4 TEM image of 10-bilayers of an a-SiC/a-Si superlattice structure.

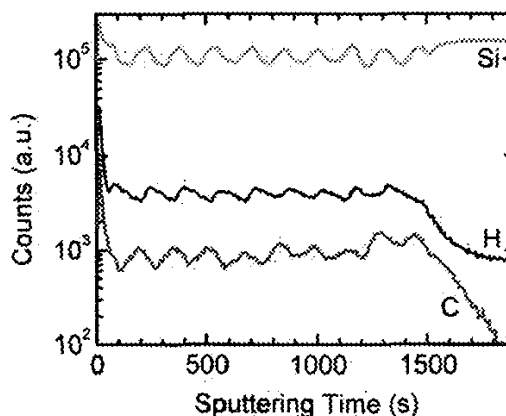


Fig. 5 SIMS spectra of the 10-bilayer a-SiC/a-Si superlattice for silicon (Si), hydrogen (H) and carbon (C).

The main challenge in the fabrication of 3C-SiC/Si superlattices is expected to be crystallisation of the a-SiC

layers. As previously mentioned, the inert nature of SiC requires extremely high processing temperatures – much higher than the melting point of silicon, in fact, and full crystallisation of the 3C-SiC is not expected until temperatures of 1800°C are reached [5]. In addition, experience with SiO<sub>2</sub>/Si superlattices has demonstrated that the crystallisation temperatures required for a-Si layers are significantly greater as the thickness becomes less than 3 nm [11].

Our hypothesis is that the a-Si will crystallise first, and subsequently, each a-SiC layer will be sandwiched between two microcrystalline silicon ( $\mu$ c-Si) layers. It is known that the growth of 3C-SiC is favoured over other  $\alpha$ -SiC polytypes when using silicon substrates [5] and since the heat of formation of 3C-SiC is lower than  $\alpha$ -SiC it is anticipated that the outer  $\mu$ c-Si layers will assist in the crystallisation of the a-SiC layers. With SiO<sub>2</sub>/Si superlattices, the SiO<sub>2</sub> is an amorphous material and does not provide a seeded crystallographic preference [11], however it is anticipated that with two materials that exhibit a crystalline phase the growth of the 3C-SiC polycrystalline film will be supported on the Si surface. Crystallisation techniques to be examined include solid phase crystallisation, rapid thermal processing, and excimer laser-based processing.

#### 4. LUMINESCENCE OF BORON-DOPED 3C-SiC

Research performed in the 1960s and 1970s has shown that boron-doped silicon carbide of all polytypes, including 3C-SiC, luminesce brightly [12,13,14]. In fact, and the first blue light emitting diodes (LED) were made of 3C-SiC. This evidence of radiative recombination occurring in 3C-SiC is significant for IPV devices, as radiative processes are known to be generally weak in indirect semiconductors. The radiative recombination process has been shown to occur via the nitrogen-boron (N:B) donor-acceptor pair (DAP) [12,13]. The luminescence spectra of a nitrogen- and boron-doped 3C-SiC (3C-SiC:B,N) single crystal is plotted in Figure 6 [12]. It can be seen that the luminescence, centred at 1.45 eV ( $\lambda = 855$  nm) is broadened due to phonon interactions.

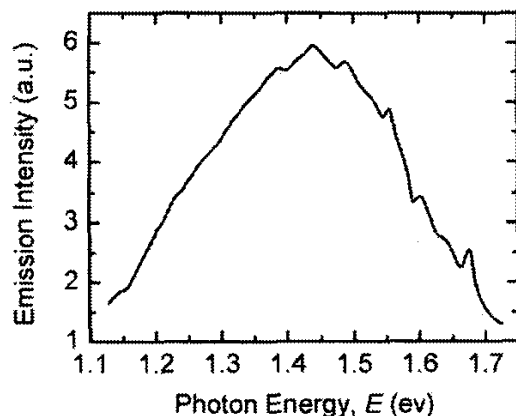


Fig. 6 Luminescence spectrum of a 3C-SiC:B,N single crystal [12].

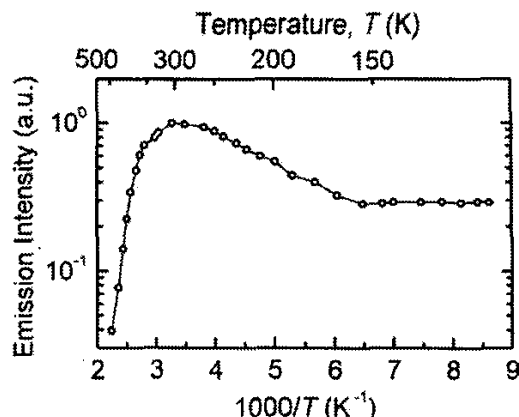


Fig. 7 Luminescence of 4H-SiC:B,N single crystal reaches a maximum at room temperature [13].

In addition, research has shown that the luminescence of the N:B pair reaches a maximum at just above room temperature, as plotted in Figure 7 for a different polytype, 4H-SiC [13]. Similar luminescence behaviour has been observed in 3C-SiC:B,N [12]. The external quantum efficiency (EQE) of the 3C-SiC:B,N luminescence at room temperature has been determined experimentally to be 18% for a single crystal [14].

The theoretical conversion efficiency predicted for a realistic IPV device based on 3C-SiC:B,N is 38%, assuming that the impurity level is 100% radiatively efficient [4]. Strikingly, if this criterion is relaxed to 0.5% radiative efficiency, an IPV solar cell with a conversion efficiency of greater than 30% can still be achieved [4]. However, in addition to radiative transitions from the valence band and donor level to the acceptor level, an IPV device would also require a radiatively efficient transition to occur from the acceptor level to the conduction band ( $E \sim 0.735$  eV). There have been no reports of such infrared luminescence in the literature.

In this work, 1  $\mu$ m- and 4  $\mu$ m-thick 3C-SiC films have been deposited onto one-side polished, [100] Si wafers cut 1° off-axis towards <110> using APCVD. The 1  $\mu$ m-thick films were planar, while the 4  $\mu$ m-thick 3C-SiC films exhibited a rough surface texture. This texture was not removed, due to its ability of enhancing the absorption, and therefore emission, of light. The films were *n*-type with a nitrogen concentration of about  $5 \times 10^{18}$  cm<sup>-3</sup>. Subsequently, a 100 – 120 nm-thick SiO<sub>2</sub> layer was grown on the 3C-SiC surface during a 4 hr wet-oxidation at 1150°C. Subsequently, five 3 cm  $\times$  3 cm pieces of the 4  $\mu$ m-thick 3C-SiC films were ion-implanted with boron at a temperature of 500°C. Higher ion-implantation temperatures have been used in the past to avoid amorphisation of the crystalline material during ion-implantation [5]. The range of boron concentration ( $10^{17}$  –  $10^{20}$  cm<sup>-3</sup> over a 0.3  $\mu$ m-deep region, beginning 0.1  $\mu$ m below the top surface) was chosen so that it would be possible to confirm the results of Suzuki *et al.*, where the ideal boron concentration was estimated to lie at levels just above that of the nitrogen background doping of the 3C-SiC material [13].

As an alternative method to obtaining 3C-SiC:B material, 1  $\mu\text{m}$ -thick, boron-doped, amorphous silicon carbide (a-SiC:B) films were deposited on quartz and polished Si wafers using PECVD. Subsequent crystallisation of the samples was performed using an 15 W excimer laser (KrF  $\lambda = 248\text{nm}$ ) in a nitrogen ( $\sim 600$  Torr) ambient. The beam area was approximately  $3\text{cm} \times 0.8\text{cm}$  with a fluence of 300 mJ. Higher fluences (up to 1050 mJ) and lower nitrogen partial pressures both resulted in the appearance of a plasma with each laser pulse, indicating that material was being ablated. A slight reduction in nitrogen pressure during the crystallisation of the six samples loaded in the vacuum chamber indicated an incorporation of nitrogen into the film.

Photoluminescence (PL) experiments were performed on all boron-doped 3C-SiC material to determine whether, firstly, the 1.45 eV DAP luminescence peak and, secondly, the 0.735 eV boron to valence band transition could be observed. The excitation source in the PL setup was a violet (406 nm, 30 mW) laser diode, while an Oriel MS260i spectrometer and a North Coast liquid nitrogen cooled InGaAs detector were used for detecting the PL signal.

Unfortunately no PL signal was obtainable from any of the APCVD-deposited and ion-implanted 3C-SiC films or the PECVD-deposited a-SiC films that underwent laser crystallisation. It was thought that the ion-implanted region may still be damaged and that non-radiative recombination mechanisms were the limiting factor. Therefore, the five samples APCVD samples were each cut into three  $3\text{cm} \times 0.8\text{cm}$  strips and KrF laser annealing (1050mJ fluence) was performed. However, this did not result in any improvement.

We anticipate that there are still too many damaged regions, including poor quality interfaces and poorly passivated surfaces. This provides a rapid recombination path for carriers within one diffusion length away from the defect, resulting in the luminescence being inhibited. Agreement with this hypothesis can be found in the literature, with B:N luminescence having only been observed in single crystals grown from the melt [12–14], and not from thin films. In addition, other researchers have observed that luminescence resulting from the nitrogen increases with film thickness [5,15]. The first 1 – 4  $\mu\text{m}$  of 3C-SiC film is often a transition region, which experiences interface misfit strain [5]. Therefore, further efforts will be directed towards obtaining higher quality 3C-SiC:B,N films and then repeating the PL experiments described here.

## 5. CONCLUSIONS

3C-SiC would appear to be good choice for certain Third Generation PV devices due to it being a group IV semiconductor with a wide bandgap. 3C-SiC films can be epitaxially grown on Si wafers using CVD, and then subsequently processed in a similar manner to Si wafers. We are currently exploring two ideas: 1) 3C-SiC/Si superlattice structures as a material with a suitable bandgap to act as an upper cell for a tandem device; 2) luminescence resulting from 3C-SiC:B,N for intended application in IPV devices. However, further work in this

area will be required as no PL signal has been observed from these thin films to date.

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