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Cubic silicon carbide as a potential photovoltaic material

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ABSTRACT

In this work we present a significant advancement in cubic silicon carbide (3C-SiC) growth in terms of crystal quality and domain size, and indicate its potential use in photovoltaics. To date, the use of 3C-SiC for photovoltaics has not been considered due to the band gap of 2.3 eV being too large for conventional solar cells. Doping of 3C-SiC with boron introduces an energy level of 0.7 eV above the valence band. Such energy level may form an intermediate band (IB) in the band gap. This IB concept has been presented in the literature to act as an energy ladder that allows absorption of sub-bandgap photons to generate extra electron–hole pairs and increase the efficiency of a solar cell. The main challenge with this concept is to find a materials system that could realize such efficient photovoltaic behavior. The 3C-SiC bandgap and boron energy level fits nicely into the concept, but has not been explored for an IB behavior.

For a long time crystalline 3C-SiC has been challenging to grow due to its metastable nature. The material mainly consists of a large number of small domains if the 3C polytype is maintained. In our work a crystal growth process was realized by a new approach that is a combination of initial nucleation and step-flow growth. In the process, the domains that form initially extend laterally to make larger 3C-SiC domains, thus leading to a pronounced improvement in crystalline quality of 3C-SiC. In order to explore the feasibility of IB in 3C-SiC using boron, we have explored two routes of introducing boron impurities; ion implantation on un-doped samples and epitaxial growth on un-doped samples using pre-doped source material. The results show that 3C-SiC doped with boron is an optically active material, and thus is interesting to be further studied for IB behavior.

For the ion implanted samples the crystal quality was maintained even after high implantation doses and subsequent annealing. The same was true for the samples grown with pre-doped source material, even with a high concentration of boron impurities.

We present optical emission and absorption properties of as-grown and boron implanted 3C-SiC. The low-temperature photoluminescence spectra indicate the formation of optically active deep boron centers, which may be utilized for achieving an IB behavior at sufficiently high dopant concentrations. We also discuss the potential of boron doped 3C-SiC base material in a broader range of applications, such as in photovoltaics, biomarkers and hydrogen generation by splitting water.

1. Introduction

The solar cell market is today dominated by single junction silicon solar cells with up to 91% of the global production with respect to power output. The single junction entails that the cell can only convert a fraction of the solar spectrum into electrical

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current, limiting its maximum theoretical efficiency at around 29% in the case of silicon. The efficiency can be increased by stacking several materials with increasing bandgap on top of each other to create a multiple junction solar cell. However, these combined material structures are typically too expensive for the general market and used mostly in niche markets, like space exploration. An attractive alternative concept is to create a metal-like intermediate band (IB) in the band gap (Eg) of a semiconductor by energy levels which form a band [1] or achieve extra carrier generation by impurity doping [2]. This would allow for a larger part of the solar spectrum to contribute to the electrical current since the IB would to utilize photons that have lower energy than Eg. In this concept, first a sub-Eg photon generates an electron that is excited from the valence band to the IB, and a second sub-Eg photon excites the electron from the IB to the conduction band. This generates additional electron–hole pairs to the ones given by absorption of photons which generate electrons from the valence band to the conduction band. In total, the efficiency of a solar cell can increase substantially.

There are several material candidates for such IB behavior [3], but most are still struggling with growth conditions and/or finding appropriate deep levels which could create an efficient photovoltaic material. Cubic SiC (3C-SiC) is unique among other candidates as it combines nearly ideal bandgap for an IB solar cell (Eg$\sim$2.3 eV) with excellent electronic properties and readily available deep centers. In particular, it can be doped with boron that introduces an energy level of 0.7 eV above the valence band [4]. An early attempt to use 3C-SiC for the increased carrier generation by boron doping was presented in 2003, but the material quality of 3C-SiC at that time was not sufficient [5]. To circumvent this limiting factor, we have developed a sublimation epitaxial growth approach that applies a lower ($<2000\,^{\circ}$C) growth temperature in comparison to the physical vapor transport (PVT) method that is generally used to produce hexagonal silicon carbide (6H- and 4H-SiC). The growth is carried out in vacuum and ensures an efficient transfer of vapor and dopant species from the source to the substrate. Our 3C-SiC growth approach allows us to control initial nucleation of 3C-SiC domains which laterally enlarge and completely cover the substrate surface [6]. Thereby a 3C-SiC material with very few domains is formed and a high crystalline quality is achieved.

The growth of 3C-SiC has for long been challenging due to its metastable nature. The 3C-SiC nucleation is not fully understood, but may be attributed to the supersaturation, concentration of various impurities, polarity of the substrate or influence of crystallographic defects. In general, the highest yield of 3C-SiC has been obtained by growth on nominally on-axis 6H or 4H-SiC substrates. On such substrates the growth proceeds via a spontaneous two-dimensional nucleation of 3C-SiC domains and their enlargement [7]. In this case the control of initial nucleation of 3C-SiC and polytype stability is very difficult. The 3C-SiC domains having different rotations can nucleate all over the surface leading to formation of high density of structural defects. The advantage is that 3C-SiC forms in a high yield and 100% could be obtained without any inclusions of the on-axis substrate polytype [7]. However, it is a pronounced challenge to obtain large domains, and domain sizes were less than a millimeter even though some growth parameters could influence the lateral domain expansion [8]. A new 3C-SiC growth approach on off-oriented 4H-SiC allows controlling initial nucleation of 3C-SiC and significantly reduce the density of structural defects [6]. Moreover, it has been demonstrated that this approach allows very high polytype stability and excellent reproducibility.

In this paper we have used two approaches to introduce boron into crystalline 3C-SiC: (i) boron doping during homoepitaxy on seeds; (ii) ion implantation. The materials are studied by optical methods to estimate the potential of 3C-SiC as intermediate band material.

2. Material and methods

The sublimation growth of 3C-SiC was performed in a graphite crucible heated by RF generator at a frequency of 46 kHz. At elevated temperatures vapor species (mainly Si, Si_2C and SiC_2) sublime from an undoped polycrystalline (ceramic) source wafer and are transferred to the substrate where they form the SiC film. The driving force for such transfer is a temperature gradient between the source and the substrate. It has been shown that this type of sublimation epitaxial configuration may reach a very high growth rate (up to 2 mm/hr at temperatures up to 2000 °C) [8]. Such growth rates are attractive for a production of 3C-SiC material for photovoltaics. In our case, we have used a moderate growth rate but high enough to prepare a free standing nominally undoped 3C-SiC substrate [6] for ion implantation or subsequent homoepitaxial growth using a boron doped source. In the latter case the boron doped polycrystalline source materials were fabricated using a PVT bulk method with a mixture of boron carbide powder and SiC carbide powder. Wafers were prepared from the boules and used as boron doped source material for the homoepitaxial growth of 3C-SiC layers on the previously grown 3C-SiC free standing material in a subsequent sublimation epitaxial process. This source preparation process is explained in detail elsewhere [9].

Transmittance measurements were performed at room temperature using UV–vis spectrophotometer and the results were used to derive the optical absorption properties. Photoluminescence (PL) measurements were carried out by employing a continuous wave HeCd laser with a wavelength of 325 nm as an excitation source. The emission was collected by a microscope and analyzed with a spectrometer system with minimal resolution 0.2 nm. The PL measurements were performed at 10 K temperature using closed-cycle He-refrigerator. Transmission electron Microscopy (TEM) was used for atomic scale crystallography analysis.

3. Results and discussion

The improvement in 3C-SiC material quality when going from on-axis growth to off-axis growth can clearly be seen from the comparison of corresponding optical micrographs in Fig. 1. On the left hand side the on-axis deposited 3C-SiC sample has formed numerous small domains that would be detrimental to any electronic devices formed on it. On the right hand side, a sample that was grown on 4° off-axis surface formed only 2–3 large domains which would expect to yield significantly improved material quality and electrical performance as was indicated in Ref. [10].

The 3C-SiC is well known for its tendency to generate stacking faults to release energy [11]. This creates a pronounced challenge in growth of material with high crystalline quality. Due to the considerable thickness of the 3C-SiC samples, there are bulk-like features of various macroscopic crystal defects. However, the TEM image in Fig. 2 clearly shows that crystallographic perfection is possible to achieve. A forthcoming main challenge in the growth process is to achieve this for a large part of the sample.

For long it has been unclear if 3C-SiC could be grown in similar quality like hexagonal 6H and 4H-SiC which are commercially available. In previous work, we have demonstrated that 3C-SiC of sufficient quality can be grown to obtain high carrier lifetime. The lifetime is one of the key parameters governing the electronic and optoelectronic devices, and it is very sensitive to the crystal