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Silicon nanocrystals produced by solid phase crystallisation of superlattices for photovoltaic applications

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ABSTRACT

Silicon nanocrystals in a dielectric matrix can form a material with higher band gap than that of bulk crystalline silicon and can therefore be applied as stable top solar cells for an all-silicon based tandem solar cell. In this review article we focus on one proven method to fabricate such structures, the superlattice approach, as cost-efficiency seems to be possible which is essential for photovoltaic applications. We comprehensively discuss the different challenges for competing material systems such as SiO_2, Si_3N_4 and SiC and give an overview on what is known so far in terms of electro-optical performance of the materials. So far, devices using silicon nanocrystals have been realised either on silicon wafers, or using in-situ doping in the superlattice deposition which may hinder the nanocrystal formation. Nevertheless, V_{oc} of up to 518 mV has been shown on such devices. In this paper we also present a membrane structure which allows the investigation of the electrical and photovoltaic properties of nanocrystal quantum dot layers independently from the substrate and unaffected by dopant diffusion. The device structure provides full flexibility in the material choice of both, i.e. electron and hole, contacts.

1. Introduction

Silicon nanocrystals are a promising candidate for the top cell of an all-Si tandem solar cell, with a band gap from 1.3 to 1.7 eV, tuneable by adjusting quantum dot (QD) size. For tandem solar cells, the Shockley–Queisser limit is raised from 31% to 42.9% (two cells), or 49.3% (three cells) for operation under diffuse light [1]. However, besides the potential efficiency improvement the implementation of such nanostructures has to fulfil a basic requirement of photovoltaic (PV) processing which is high throughput at low cost. Therefore we will focus this literature review on just one preparation method which clearly fulfils the requirements and is therefore in the major focus of today's R&D work on Si QDs for PV.

This method is the formation of Si QDs within a host material by solid phase crystallisation as pioneered exemplarily in SiO_2 by Zacharias et al. [2]. It involves depositing a multilayer consisting of alternating layers of silicon-rich and stoichiometric layers of a silicon-based dielectric such as SiO_2, Si_3N_4, or SiC [3]. The silicon-rich dielectric phase-separates into stoichiometric dielectric and c-Si on thermal annealing [4]:

$$Si(O, N, C)_x \rightarrow (x/2) \times Si(O_2, N_{4/3}, C) + (1 - x/2) \times Si \quad (1)$$

The size of the Si domains can in principle be constrained in one direction by keeping the silicon-rich layers suitably thin and in all other directions by tuning the composition of the silicon rich layer (see Fig. 1). The extent to which this control is achievable in the different dielectrics is reviewed later.

The choice of dielectric has a large impact on carrier transport and absorption in the Si QD layers. As the dielectrics exhibit large band offsets to the Si QDs conduction is expected to be via interdot tunnelling [5]. Fig. 2 shows band offsets to bulk crystalline Si. These decrease for QDs as QDs have a bigger band gap than bulk Si [6]. SiC exhibits the smallest band offsets, resulting in the highest expected mobility of carriers for a given QD size and separation [7] (see Fig. 3).

The calculation underpinning Fig. 3 was carried out with estimated values for the effective mass and carrier lifetime. While the exact values are therefore perhaps not particularly accurate, the trend is valid and shows that much more control of the interdot spacing is necessary in silicon oxide and nitride than in carbide. Within the same work, it was also determined that dot size primarily affects the position of QD energy bands, while their width is affected by the matrix barrier height – lower barrier heights lead to wider bands [5]. An anisotropic carrier effective mass was found to reduce the gaps between QD energy bands. Wide bands with small gaps are viable for solar cells as they increase the range of

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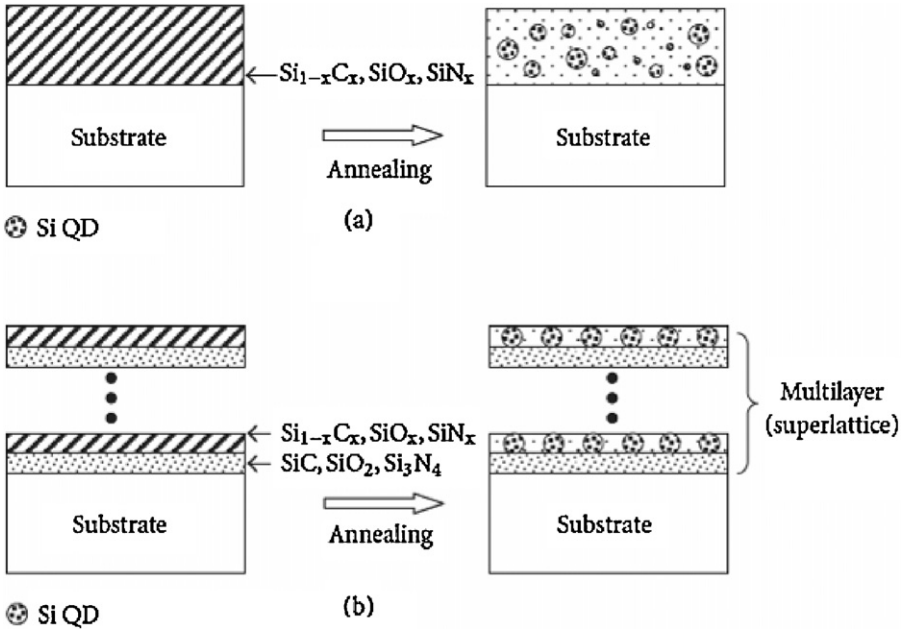

Fig. 1. Schematic of phase separation in silicon-rich dielectrics on annealing (from [4]). Using a multilayer with controlled layer thicknesses (b) should permit better control of Si QD size and spacing than using a single silicon-rich dielectric layer (a).

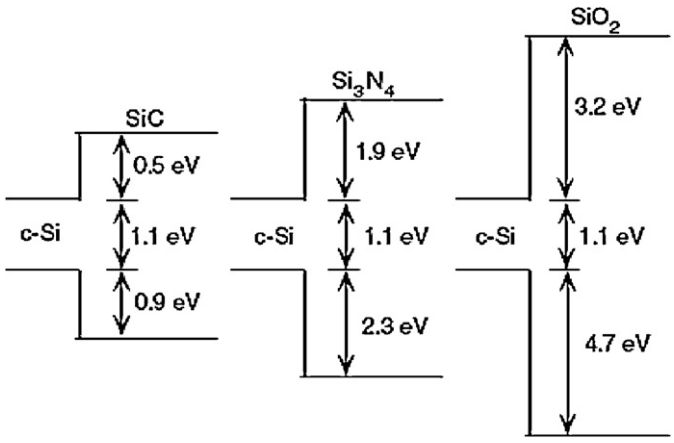

Fig. 2. Band offsets between Si-based dielectrics and c-Si (from [6]).

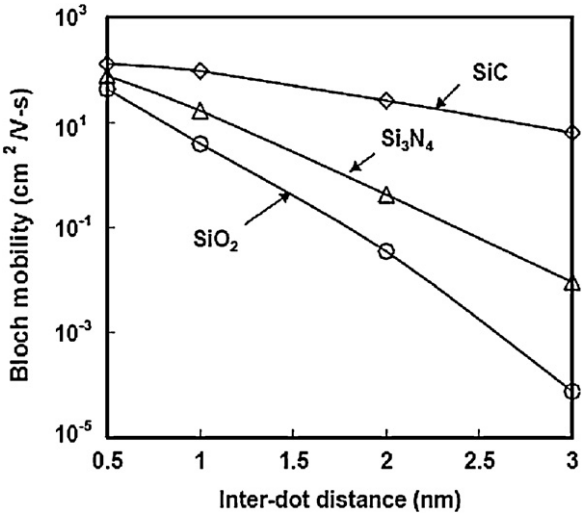

Fig. 3. Theoretical mobility of carriers in Si QD/dielectric films (from [7], 2 nm × 2 nm × 2 nm cubic QDs assumed).

photon energies that can be absorbed. Absorption, together with the minority carrier lifetime, determines the excess carrier density created in a solar cell absorber, which in turn determines the short-circuit current, and, via its influence on the quasi-Fermi-level splitting, the open-circuit voltage. Löper et al. [8] calculated the quasi-Fermi-level splitting for Si QDs embedded in dielectrics by combining a density of states calculation similar to that in [5] with an estimate of the excess carrier density derived from experimental absorption and lifetime measurements. They found that the quasi-Fermi level splitting is generally 0.6 eV less than the Si QD band gap with no further dependence on matrix material or dot spacing, with a 0.24 eV increase attainable if 100 times more light could be absorbed.

2. Materials systems

2.1. Silicon quantum dots in SiO_2

SiO_2 was the first matrix material in which Si QDs with well-defined sizes could be embedded successfully. Due to its high bandgap SiO_2 is transparent to visible light. Besides that SiO_2 is known to be a potentially good passivation for the Si interfaces, making this a model system in which to study the properties of Si QDs. Si QDs in SiO_2 with a narrow size distribution were first synthesised from a multilayer structure as shown in Fig. 1 by Zacharias et al. in 2002 by evaporation of SiO powder in varying amounts of O_2 and annealing at 1100 °C in N_2 for 1 h [2]. Transmission electron microscopy (TEM) revealed a high density of monodisperse Si QDs which the authors claimed are self-organised (see Fig. 4). They also reported successful control of QD size, by adjusting the silicon-rich oxide (SRO) thickness, and QD density, by adjusting the SRO stoichiometry. QDs with a diameter less than 2 nm were found to be unstable. A blue-shift in photoluminescence spectra was measured with decreasing QD size (see Fig. 5), as is expected from quantum confinement. This was in agreement with the findings of Kanzawa et al. [9] and Takeoka et al. [10] who observed similar trends annealed sputtered silicon-rich oxide films for Si NCs with diameters below and above the Bohr exciton radius respectively.