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Electrical properties of silicon carbide/silicon rich carbide multilayers for photovoltaic applications

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ABSTRACT

Silicon carbide/silicon rich carbide multilayers, aimed at the formation of silicon nanodots for photovoltaic applications, have been studied. The electrical properties have been investigated at the nano-scale by conductive Atomic Force Microscopy (c-AFM) and at macro-scale by temperature dependent conductivity measurements. The mixture is composed of highly conductive Si nanoclusters and moderately conductive SiC nanoclusters in a disordered matrix. The conduction mechanism takes place via band states induced by the disorder at the interface between nanodot clusters. Structural properties have been extracted by optical spectroscopy analyses. The results contribute to the understanding of the microscopical electronic mechanisms of the composite material, which is a candidate for third generation photovoltaics.

1. Introduction

Efficiency increasing and cost reduction are key concepts in the development of the photovoltaic field. One of the factors responsible for power loss in single band gap solar cells is that photons with energy higher than the band gap lose their excess energy by thermalization, while photons with energy below the band gap are not successfully converted. One way to overcome this limit is to introduce the multi-junction concept, where materials with different band gap are stacked together [1,2]. In this framework, silicon nano-crystals (Si NCs) embedded in a dielectric matrix were proposed as absorbers in all-Si multi-junction solar cells due to the quantum confinement capability of Si NCs, that thanks to the size induced tunability of the band gap allows a better match to the solar spectrum [3,4]. SiC as a dielectric matrix is considered promising as it shows better conduction properties and lower barrier to the Si NCs with respect to e.g. SiO_2 [1,2].

Despites the high interest in the applications, some of the physical properties of this system remain to be elucidated. In particular, limited information exists about the electronic properties of the system. The Si NCs/SiC system is characterized by the presence of grain boundaries and residual Si and SiC amorphous phases resulting from the Si NCs formation process, which has been shown to be dominated by the high Si/SiC interface energy [5]. In view of the device applications, it is therefore crucial to establish the role of such structural defects in determining the electronic properties of the material. Few experimental studies on Si NCs/SiC films exist [5–11], and the electrical properties of such a material are not yet completely clarified.

The present contribution focuses on the electrical transport at the nano-scale in Si NCs embedded in a SiC matrix (Si NCs/SiC). Such system has already been proposed for application to all-Si based tandem solar cells [10,12].

The material has been obtained by means of the superlattice approach [13] using Plasma Enhanced Chemical Vapor Deposition (PECVD) of SiC/Silicon Rich Carbide (SRC) multilayers followed by high temperature annealing. Correlation with macroscopic electrical transport is attained by taking into account the layer composition deduced by fitting the Reflectance and Transmittance (R&T) spectra in the UV–vis. Variation in conductivity at the nano-scale is investigated by conductive Atomic Force Microscopy (c-AFM): a conductive probe is put in contact with the surface and the current flowing between the tip and the sample is measured at constant bias [14]. This approach gives a fundamental insight on the electrical properties of Si NCs/SiC mixtures.

Amplitude modulation AFM (tapping mode) is performed in order to obtain high resolution topographical imaging [15] and phase contrast mapping, which provides information on the power dissipated between the tip and the surface [15].

The electrical conductivity has been measured as a function of temperature in order to study the electrical transport mechanism of the system. If σ is the conductivity and T the temperature, σ as a function of T can be expressed as:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \quad (1)$$

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where σ_0 is the conductivity prefactor and E_a is the activation energy. Typically, disordered systems show an exponential relationship between σ_0 and the activation energy E_a, known as the Meyer–Neldel Rule (MNR) or the compensation law [16], expressed as

$$\sigma_0 = \sigma_{00} \exp\left(\frac{E_a}{E_{MN}}\right) \quad (2)$$

with E_{MN} and σ_{00} MNR constants which are typical signature of a system. The conductivity mechanism has been investigated by comparing the measured MNR constants with values reported in literature for Si based disordered systems. The comparison between macroscopical and microscopical conductivity analyses has allowed us to propose a model for the electrical conduction in SiC/SRC multilayers.

2. Materials and methods

SiC/SRC multilayers (ML) were deposited by PECVD on quartz. The precursor gases used are SiH_4, CH_4 and H_2, the temperature of the substrate is 325 °C. The multilayers are composed of a stack of 30 bi-layers of SRC and SiC. The silicon fraction in the SRC layers is 0.85. The thickness of the as-deposited layers is 9 nm for SiC (d_{SiC}) and varies between 2 and 4 nm for SRC (d_{SRC}). A sacrificial a-Si:H layer (20 nm thick) was deposited on top of the multilayer structure in order to prevent SiC surface oxidation during the subsequent annealing for Si and SiC NCs formation [13], which was performed at 1100 °C for 30 min in flowing N_2 and 10% O_2. Reference single layers a-SiC:H and a-Si:H were deposited for comparison: nc-SiC and nc-Si were produced by annealing at 1100 °C, a-SiC and a-Si by dehydrogenation at 600 °C. The preparation of all samples was completed by wet etching of the sacrificial layer as described in [17].

Parallel Ni pads were deposited by thermal evaporation for current–voltage measurements. A dry etching (SF_6+O_2, 20 s) was used to remove the shallowest 5–10 nm from the surface before local conductivity measurements. In all cases the SiC-rich surface was effectively thinned. The thickness of the dry-etched layer was measured by fitting the R&T spectra of the layers before and after the etching treatment.

R&T spectra were acquired in the UV–vis range by an Avantes fiber optics spectrophotometer and fitted by the software Optical [18]. The simulations use the refractive index spectra of SiC and a-Si as determined by fitting [19] and the reference single SiC and a-Si layers, whereas the optical function of Si NCs were approximated using the literature function of continuous nc-Si [20].

Current–voltage curves as a function of temperature are measured in order to obtain the lateral conductivity of the multilayers and the temperature varies between 27 and 100 °C. AFM was used both in tapping and contact mode to measure the surface topography, the energy dissipation between the tip and the sample and the local conductivity. In order to obtain the latter, a conductive Pt coated tip is used, with nominal radius of curvature of 35 nm (NT-MDT CSG10/Pt). The microscope used is a NT-MDT Solver P47H Pro.

3. Results and discussion

Preliminary structural characterization studies of the layers analyzed in this study is reported elsewhere [5,11]. Using Energy Filtered Transmission Electron Microscopy (EFTEM), High Resolution TEM (HRTEM), X-ray diffraction (XRD), Raman scattering, and Fourier Transform Infrared Spectroscopy (FTIR), the formation of Si NCs surrounded by an amorphous tissue is evidenced. The SiC matrix shows a 63% crystallized fraction in form of 3C–SiC NCs of about 3 nm diameter. Details on sample characterization and discussion on the physical origin of the obtained material can be found in [5].

The fitting of the R&T spectra by means of the Bruggeman Effective Medium Approximation (EMA) [21] also gives quantitative information on the nc-Si, a-Si and SiC relative volumes, provided that the optical functions (n, k) of the components are known.

An example of simulation for the ML with 4 nm SRC on quartz is reported in Fig. 1a. Nominal R&T spectra expected for varying SiC/a-Si/nc-Si composition are reported in Fig. 1b.

The R&T spectra can be qualitatively interpreted by distinguishing three regions: region A (high absorption, $T=0$), region B (low absorption, $T\neq 0$, $R+T<100\%$), and region C (transparency: $R+T=100\%$). In regions B and C, the interference of light reflected at the surface and at the interface with the substrate gives rise to an oscillating pattern.

In region C, the fringe contrast is determined by the refractive index contrast between the multilayer and substrate. Such peculiarity allows us to determine the SiC-to-Si ratio. This is also illustrated in Fig. 1b, where the crystallized fraction X_c (defined as the ratio between the nanocrystallized-to-total Si volume) is fixed and the SiC-to-Si ratio is varied. The figure shows that the fringe contrast increases with decreasing SiC volume fraction, as a consequence of the lower refractive index of the mixture. The determination

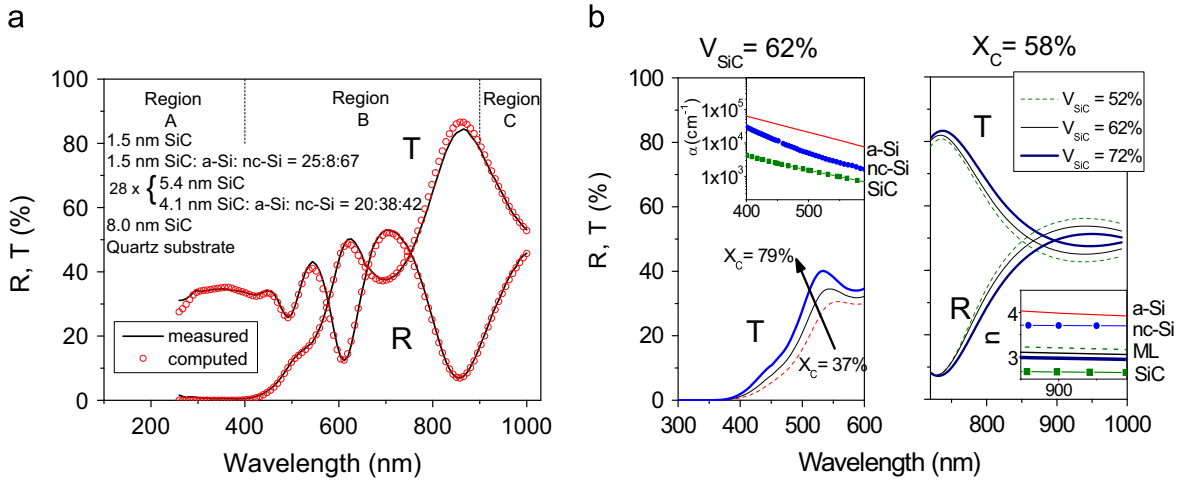

Fig. 1. (a) Measured (lines) and simulated (symbols) R&T spectra of a ML sample with $d_{SRC}=4$ nm. The simulation is obtained using the complete ML structure including surface and buffer layers as indicated in the figure. (b) Computed spectra of 220 nm film/quartz, for different SiC/a-Si/nc-Si compositions of the film. On the left: SiC=62%; X_c=37–79%. On the right: X_c=56%; SiC=52–72%. X_c represents the crystallized fraction.

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