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Identification and tackling of a parasitic surface compound in SiC and Si-rich carbide films

M. Canino[a,*], C. Summonte[a], M. Allegrezza[a], Rimpy Shukla[a,b], I.P. Jain[b], M. Bellettato[a], A. Desalvo[a], F. Mancarella[a], M. Sanmartin[a], A. Terrasi[c], P. Löper[d], M. Schnabel[d], S. Janz[d]

[a] CNR-IMM, via Gobetti 101, 40129 Bologna, Italy
[b] Centre of Non-Conventional Energy Resources, University of Rajasthan, Jaipur, India
[c] CNR-IMM, via Santa Sofia 64, 95123 Catania, Italy
[d] Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, 79110 Freiburg, Germany

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ABSTRACT

Silicon carbide and silicon rich carbide (SiC and SRC) thin films were prepared by PECVD and annealed at 1100 °C. Such a treatment, when applied to SiC/SRC multilayers, aimed at the formation of silicon nanocrystals, that have attracted considerable attention as tunable band-gap materials for photovoltaic applications. Optical and structural techniques (X-ray photoelectron spectroscopy, Reflectance and Transmittance, Fourier Transformed Infrared Spectroscopy) were used to evidence the formation, during the annealing treatment in nominally inert atmosphere, of a parasitic ternary SiO_xC_y surface compound, that consumed part of the originally deposited material and behaved as a preferential conductive path with respect to the nanocrystal layer in horizontal electrical conductivity measurements. The SiO_xC_y compound was HF-resistant, with composition dependent on the underlying matrix. It gave rise to a Si-O related vibration in FTIR analysis, that may be misinterpreted as due to silicon oxide. The compound, if neglected, can affect the structural and electrical characterization of the material.

To overcome this problem, a procedure is analyzed, based on the deposition of a sacrificial capping a-Si:H layer that partially oxidizes, and is removed by tetra methyl ammonium hydroxide (TMAH) after annealing. XPS analysis revealed that the resulting surface is mainly made up of SiC regardless of the composition of the underlying SRC layer. Subsequent SF_6:O_2 dry etching results in a porous SiC-rich surface layer. The proposed method is effective in controlling the SRC surface configuration, and allows the performance of reliable optical and electrical characterization.

1. Introduction

Silicon nanocrystals (Si-nc) have attracted strong interest in view of the development of silicon-based third generation solar cells. The possibility of tuning the Si bandgap with size scaling makes Si-nc suitable as absorber material for the top solar cell of a tandem structure [1]. Si-nc embedded in a silicon carbide (SiC) matrix can show both quantum confinement and good electrical transport [1]. The preparation of such material by the multilayer approach, as proposed for Si-nc in SiO_2 by Zacharias et al. [2], requires high temperature annealing to promote phase separation, Si crystallization and good electrical quality of the matrix [3,4]. In some cases, as a consequence of high temperature annealing, a surface ternary compound SiO_xC_y or a mixture of Si-, C-, and O-based phases is detected [5], even though the annealing is often performed in nominally inert atmosphere. These complexes are evidenced by the presence of the characteristic Si-O signal in FTIR spectra [6–8], and are often mistaken for SiO_2, though in some cases they are not removed by wet etching [9]. The presence of a defective surface compound has likely an effect on the electrical performance of the obtained material.

In this work surface reactions with oxygen leading to undesired surface oxidation have been prevented by protecting the surface with an a-Si:H encapsulation, as proposed also by Schnabel et al. [10]. The effectiveness of the proposed treatment has been analyzed in terms of optical (reflectance and transmittance, R&T), structural (X-ray photoelectron spectroscopy, XPS) and electrical (lateral conductivity) properties of the produced SiC and Si-rich carbide layers.

2. Experimental

2.1. Sample preparation

Several Si-rich carbide layers, Si_xC_{1-x}, with Si excess x ranging between 0.5 (stoichiometric SiC) and 0.75, were produced by

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[*] Corresponding author. Tel.: +39 051 639 9127; fax: +39 051 639 9216.
E-mail address: canino@bo.imm.cnr.it (M. Canino).

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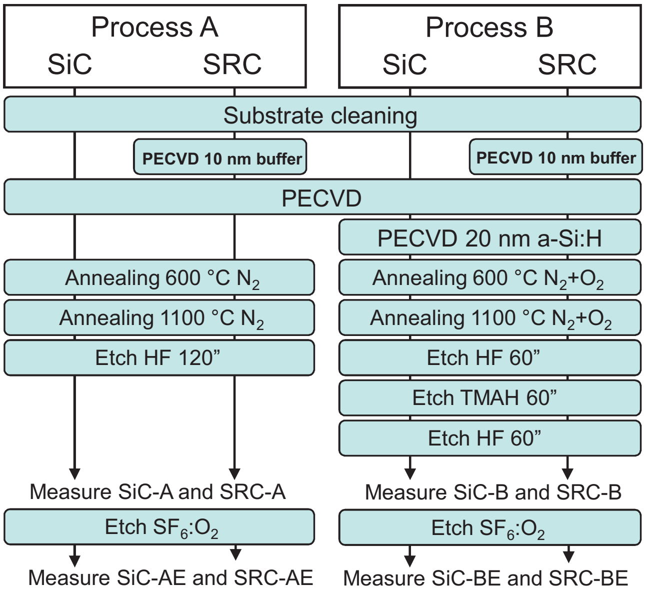

Fig. 1. Comparison between the production sequences (a) and (b).

Plasma Enhanced Chemical Vapour Deposition (PECVD) both on quartz and on double-polished FZ c-Si substrates. All layers were deposited at 350 °C in a plasma of SiH_4, H_2 and CH_4, at 13.56 MHz frequency and 4 W power. Different x were obtained by changing the SiH_4/CH_4 flow ratio, whereas the H_2 flow was kept constant at 10 sccm. The SiH_4/CH_4 flow ratios were equal to 2.6/70 for stoichiometric SiC, 6.1/70 for $x = 0.65$ (this composition from now on will be referred to as SRC), and 11.4/70 for $x = 0.75$. In the case of $x = 0.65$ and $x = 0.75$, a 20 nm thick SiC buffer layer was inserted between the Si_xC_{1-x} and the substrate to prevent epitaxial growth of the excess Si from the c-Si substrates.

Two series of SiC and SRC, were produced according to two different procedures, named A and B. The production sequence of both sets of samples is summarized in Fig. 1. Process A was a “standard” treatment, consisting in dehydrogenation at 600 °C for 4 h and annealing at 1100 °C for 30 min in N_2 (O_2 contamination <2 ppm). After annealing the samples underwent an etching in $HF:H_2O = 1:10$ for 120 s. The samples produced using this treatment are labelled SiC-A and SRC-A.

Process B was optimized with the aim of minimizing SiO_xC_y formation. The samples that underwent the B treatment are labelled SiC-B and SRC-B, and consist of SiC and SRC layers, initially as thick as their A equivalents, encapsulated with a 20 nm thick a-Si:H layer, deposited from a plasma of undiluted SiH_4. They underwent an annealing equal in duration and ramps to the one of process A, except that, in the annealing atmosphere of process B, 10% O_2 was added to the flowing N_2 to provide a controlled oxygen supply to the material. The post annealing wet etching treatment was: (i) $HF:H_2O = 1:10$ 60 s, to remove the surface oxide; (ii) diluted tetra methyl ammonium hydroxide ($TMAH:H_2O = 2:100$) at 40 °C 60 s, to remove the residual Si encapsulation; (iii) $HF:H_2O = 1:10$ 60 s. After the removal of the SiO_2 layer (i), the sample surface was hydrophobic indicating that an unreacted Si layer was still present. After the Si removal (ii, iii) the surface was hydrophilic, indicating the removal of the surface Si.

As a consequence of the B treatment the surface of SRC-B turned out to be rich in SiC. In order to remove either the surface compound observed on SiC-A and SRC-A, or the SiC-rich layer from SRC-B, all the samples underwent a $SF_6:O_2$ dry etching treatment, with 64:22 (flows in sccm) gas flow ratio, at 75 mTorr, 80 W. The plasma chemistry is suitable for controlled SiC etching [11]. The etch rate on Si_xC_{1-x} showed a marked dependency on composition and was determined to be 23 nm/min for stoichiometric SiC, 40 nm/min for $Si_{0.65}C_{0.35}$, and around 700 nm/min for c-Si [12]. This dry etching treatment is supposed to have nonzero etch rate for SiO_2, but the exact value was not determined. The etching durations were chosen in order to remove 20–30 nm from the top of each sample. The names of the samples after dry etching end with “E”.

As a preliminary experiment some a-Si:H and $Si_{0.75}C_{0.25}$ layers, with no encapsulation, were annealed either in N_2 or in $N_2 + O_2$ for different times, in order to verify the necessity of the Si encapsulation to avoid incomplete Si_xC_{1-x} oxidation and to calibrate the a-Si:H oxidation rate.

2.2. *Characterization*

R&T spectra were measured in the range of 190–820 nm with a HP 8452A diode array spectrophotometer and in the range of 240–1000 nm with an Avantes fibre optical spectrophotometer.

The R&T spectra were simulated using the computer code Optical, that treats the multilayer structure using the Jones matrix—Fresnel coefficient approach [13], and allows the use of the Bruggeman effective medium approximation (EMA) in the description of the spectral refractive index of the layers [14].

The simulation, based on χ^2 minimization, was obtained by using a stack of 4 layers: L1: surface oxide; L2: residual microcrystalline Si, L3: Si_xC_{1-x} layer; and L4: substrate. From the analysis, we extracted the thickness of each film, and the EMA composition of L3. The materials entering the simulation were SiO_2 (spectral data from [15]), μc-Si, and a-Si (spectral data from Ref. [16]), and microcrystallized SiC. The spectral data for the latter were determined on a single SiC sample deposited on quartz and annealed at 1100 °C, and fitted by the modified Tauc–Lorentz model [17], further improved to finely account for defect excess absorption [Allegrezza, unpublished result]. The presence of surface roughness is simulated by an EMA mixture containing voids in layer L1. The error on the material fractions in the bulk of the samples is in the range ±1 to 5%, higher for higher fractions. The maximum error on total thickness is ±6 nm.

The layers on c-Si substrate were used for Fourier Transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). FTIR measurements were performed with 16 cm^{-1} resolution using a Thermo Nicolet 5700 spectrometer. The absorption spectra were taken after substrate and baseline subtraction and normalization to the sample thickness.

XPS measurements were made both in normal (80° take-off angle) and grazing (30° take-off angle) incidence (NI and GI, respectively) using an Al K_α source, with an overall energy resolution of 1.2 eV. The scan area was 1 mm^2.

Lateral conductivity measurements were performed in vacuum in the temperature range of 27–100 °C on layers deposited on quartz, with parallel plane contacts made by nickel evaporation.

3. Results

3.1. *FTIR*

Fig. 2 shows the IR absorbance of a SiC layer of set A, as annealed and after immersion in diluted HF. The peak at 800 cm^{-1} is due to Si-C stretching vibration. The Lorentzian shape confirms crystallization of SiC [6]. The peak at 1069 cm^{-1}, attributed to the Si-O stretching vibration [18], gives evidence of the formation of Si-O bonds. The characteristic peak of the Si-O stretching vibration disappears after etching in diluted HF. Thus, it is likely to be correlated to a SiO_2 layer formed during the annealing, although the annealing was performed in an inert atmosphere. However, FTIR is not a