



# Electrochemical synthesis of photoactive carbon-carbide structure on silicon in molten salt

Eimutis Juzeliūnas<sup>a,b,c,\*</sup>, Derek J. Fray<sup>a</sup>, Putinas Kalinauskas<sup>b</sup>, Ignas Valsiūnas<sup>b</sup>, Gediminas Niaura<sup>b</sup>, Algis Selskis<sup>b</sup>, Vitalija Jasulaitiene<sup>b</sup>

<sup>a</sup> Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Road, CB3 0FS Cambridge, United Kingdom

<sup>b</sup> The Centre for Physical Sciences and Technology, Saulėtekio Str. 3, Vilnius, Lithuania

<sup>c</sup> Klaipėda University, Herkaus Manto 84, 92294 Klaipėda, Lithuania

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## ABSTRACT

Carbon-carbide coatings on silicon with a distinctively developed surface were electrochemically synthesized in molten  $\text{CaCl}_2$  using  $\text{Si-SiO}_2$  precursor and a graphite anode. Energy-dispersive X-ray spectroscopy showed approximately one quarter of the structure (in at.%) was composed of carbon. X-ray diffraction identified crystalline phases of graphite, silicon carbide and carbonate. X-ray photoelectron spectroscopy identified the carbide/carbon concentration ratio varied from 0.2 in the external region of the structure to 0.7 at the silicon substrate boundary. Mott-Schottky analysis showed *p*-type semiconductivity of the structure with high density of charge carriers  $N > 10^{16} \text{ cm}^{-3}$ . The surfaces absorbed over 90% of white light in a broad region of wavelengths from 400 nm to 1100 nm. The obtained composite is promising for application as an antireflection and protective coating or a photoelectrode.

## 1. Introduction

Carbon-silicon (C-Si) coatings are promising for increasing the light harvesting performance of silicon-based solar cells. Low reflectance values were determined for diamond-like carbon/porous silicon systems over a wide energy range, which includes the UV, the visible and the infrared regions [1]. Diamond-like C-SiC system showed an increased refractive index, optical bandgap and hardness [2]. The C-SiC system improved efficiency of solar cell up to 1.5 times and SiC up to 1.3 times. A two-layer  $\text{SiO}_2/\text{SiC}$  structure on silicon enhanced the cell performance by 34.15% due to light trapping and accelerated photoelectron generation [3]. Good surface passivation and energy conversion efficiency of 17.4% was also reported for  $\text{SiC}_x\text{N}_y$  coatings [4].

Procedures of chemical or physical vapor deposition as well as various etchings are typically used to improve the antireflection performance of silicon-based solar cells. Most of these techniques, however, are not cost effective and also include hazardous reactants.

Silicon electrochemistry in molten salts attracted considerable attention mainly in attempts to extract high-purity silicon from  $\text{SiO}_2$  [5–12]. The electrochemical silica deoxidation provides a green alternative to the carbo-thermic silicon production – a process that is highly energy inefficient and harmful to the environment.

Here we show an electrochemical method of silicon surface modification by a carbon-carbide system in molten calcium chloride. The proposed method offers new opportunities for production of carbon-modified silicon surfaces for efficient photodevices.

## 2. Experimental

Anhydrous  $\text{CaCl}_2$  was kept in an evacuated oven for 3 h at 80 °C and 120 °C and 18 h at 180 °C, to remove residual water and  $\text{Ca(OH)}_2$ . The residual pressure was  $10 \pm 5 \text{ mBar}$ .

*P*-type <100> single-crystal silicon wafers with polished surfaces were used as precursors with diameters of 5 cm, area - 22.8 cm<sup>2</sup>, thickness -  $275 \pm 25 \mu\text{m}$  and resistivity 1 to 30  $\Omega \text{ cm}^{-1}$ . The samples were thermally coated by a silica layer of 300 nm thickness (from Si-Mat GmbH, Germany). Rectangular specimens 3 cm × 1 cm were attached to a Mo frame as shown previously [13].

A cylindrical alumina crucible and a vertical tube furnace (Instron SFL, UK) were used. The molten salt was held at 950 °C under an Ar atmosphere. Graphite rods, 10 mm in diameter, served both as pseudo-reference and counter electrodes. The  $\text{Si-SiO}_2$  precursor was polarized in molten salt, taken out from the reactor, rinsed in deionized water and in 0.5 M HCl to dissolve salts.

Thickness of a native silica film on silicon wafer, which forms

\* Corresponding author at: The Centre for Physical Sciences and Technology, Saulėtekio Str. 3, Vilnius, Lithuania.  
E-mail address: [eimutis.juzeliunas@ftmc.lt](mailto:eimutis.juzeliunas@ftmc.lt) (E. Juzeliūnas).

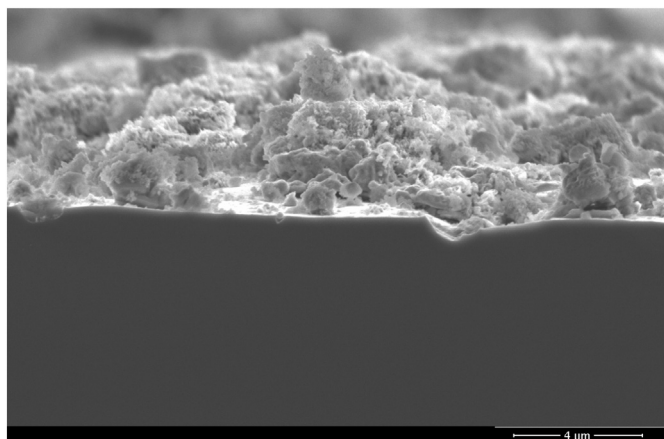


Fig. 1. a) Side view of the surface formed on silicon in molten  $\text{CaCl}_2$  at  $E = -1.25$  V vs. graphite for 20 min. Precursor – silicon wafer with 300 nm  $\text{SiO}_2$  layer.

spontaneously during polishing and exposing at ambient conditions, was estimated to be  $d \sim 0.8$  nm by the spectroscopic ellipsometry. The measurements were performed using a Sopra GES 5 ellipsometer in the range of optical spectrum 300 nm to 900 nm.

Reflectance spectra were recorded with Lambda 35 spectrometer (PerkinElmer Inc.) equipped with diffuse reflectance accessory RSA-PE-20.

X-ray photoelectron spectroscopy (XPS) experiments were performed using a “VG Escalab MK II” spectrometer from VG Scientific (UK) and X-radiation of  $\text{Mg K}\alpha$  anode. The pressure in the UHV analyzer chamber was  $1.33 \times 10^{-7}$  Pa. To obtain depth profiles,  $\text{Ar}^+$  sputter cleaning was applied with a 4 keV beam at incident angle of  $54^\circ$  relative to the surface. The sputtering current was  $100 \mu\text{A}/\text{cm}^2$ , which corresponded to the etching rate 9.0 nm/min for Si and 8.5 nm/min for  $\text{SiO}_2$ .

X-ray diffraction (XRD) measurements were performed in the  $2\theta$  range from  $5^\circ$  to  $70^\circ$  with the step size  $0.05^\circ$  using Cu anode and a Philips X’Pert PW3020 diffractometer and software.

Surfaces and compositions were also studied by a scanning electron microscope (SEM-EDX) FEI Helios Nanolab Dual Beam workstation equipped with a secondary electron detector and a focused ion beam.

Photoelectrochemical measurements were carried out in a glass cell

equipped with a quartz window using a white LED as an illumination source.

### 3. Results and discussion

Electrochemical synthesis of Si-SiC-C structure was performed at  $E = -1.25$  V vs. carbon pseudo-reference electrode. A structure with a developed surface area formed during the polarization (Fig. 1). The energy-dispersive X-ray spectroscopy (EDX) identified carbon, silicon and oxygen on the surface although some non-uniformity of distribution of these elements over the surface has been detected. The atomic percentage of carbon varied, from place to place, in the range 22.3 at.% to 28.5 at.%, that of silicon 49.2 at.% to 53.4 at.% and oxygen 23.2 at.% to 30.5 at.%.

The XRD data in Fig. 2 identified crystalline phases of silicon carbide, graphite and calcium carbonate. Note that carbonate is removable by washing the sample in acidified solution, while the rest of the structure (Si, C, SiC) is resistant to most of acids.

XPS provided analytical information on the oxidation states of elements (Fig. 3). The sample etching by argon ions ( $\text{Ar}^+$ ) has been applied to obtain depth profiles. The  $\text{Si}2p$  energy spectra in Fig. 3(a) identify oxidized silicon on the pristine surface. In deeper levels, both oxidized and non-oxidized silicon (Si and  $\text{Si}^{4+}$ ) is present. No oxidized silicon was found at the depth  $d \sim 100$  nm, this means thickness of the silica film is  $d < 100$  nm. Fig. 3b and c show  $\text{C}1s$  spectra and fitting curves with the energy peaks at 283.2 eV and 284.6 eV, which identify Si–C and C–C bonds, respectively [14]. The concentration ratio was found from spectra areas  $[\text{SiC}]/[\text{C}] = 0.2$  at the depth  $d \sim 8.5$  nm. The carbide content increased with the depth up to  $[\text{SiC}]/[\text{C}] = 0.7$  at  $d \sim 100$  nm, that is around the Si substrate boundary. Such increase is understandable: deeper levels correspond to longer interaction time between the carbon deposits and the substrate. The fitted curves identify traces of carbonate as well.

As widely discussed in literature [5–13], oxygen is released when polarizing Si- $\text{SiO}_2$  system in a molten salt due to electrochemical silica deoxygenating at three-phase interface Mo- $\text{SiO}_2$ - $\text{CaCl}_2$ .



The produced silicon is conductive at high temperature, so it forms a new interface Si- $\text{SiO}_2$ - $\text{CaCl}_2$  that spreads over the silica surface [13]. Typically, the reaction (1) leads to some surface porosity forming

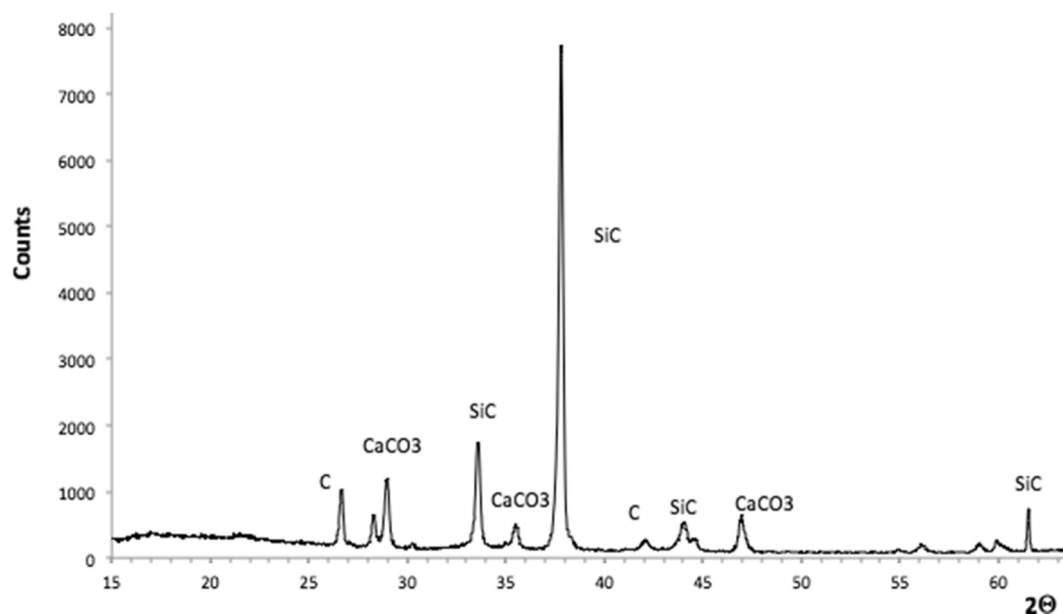


Fig. 2. XRD data obtained for the Si- $\text{SiO}_2$  sample polarized at  $E = -1.25$  V vs. graphite for 20 min.

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