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Fabrication of topographically microstructured titanium silicide interface for advanced photonic applications

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ABSTRACT

We present a widely scalable, high temperature post-growth annealing method for converting ultra-thin films of TiO_2 grown by atomic layer deposition to topographically microstructured titanium silicide (TiSi). The photoemission electron microscopy results reveal that the transformation from TiO_2 to TiSi at 950 °C proceeds via island formation. Inside the islands, TiO_2 reduction and Si diffusion play important roles in the formation of the highly topographically microstructured TiSi interface with laterally nonuniform barrier height contact. This is advantageous for efficient charge transfer in Si-based heterostructures for photovoltaic and photoelectrochemical applications.

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Titanium silicide (TiSi) nanostructures have been widely used in nano- and microelectronics as ohmic contacts and interconnect materials [1] and, in recent years, photoelectrochemical (PEC) devices developed for water splitting [2–4]. TiSi has an exceptionally broad band-gap from 1.5 eV to 3.4 eV that is alone large enough to allow photocatalytical splitting of water [4]. The efficiency of a PEC device can be increased by interfacing a semiconductor material with an electrocatalyst (EC). Key parameters in the optimization of PEC materials for water splitting are the electronic band positions with respect to water redox potentials. Under electrolyte contact, the Fermi levels of a photoelectrode and electrolyte redox species align via charge transfer resulting in band bending within the semiconductor photoelectrode. If an EC covers a semiconductor substrate completely, the electronic band alignment is determined by the EC. In contrast, if the EC layer is discontinuous, the band alignment can behave like the semiconductor but the surface has the catalytic activity of the EC. Based on the "pinch-off" theory this behavior is valid for catalyst particles with dimensions smaller than the depletion width of the semiconductor [5]. The depletion width is strongly affected by the degree of free charge carriers, and is in the range of few micrometers for a lightly doped Si [6].

Here we demonstrate a simple atomic layer deposition (ALD) and thermal annealing based method for fabricating a topographically microstructured discontinuous TiSi surface on Si substrate. This allows for energy band engineering of photoelectrodes via exploitation of the pinch-off effect. Hill et al. recently showed that the pinch-off effect produced by cobalt silicide heterostructures grown on silicon photoanodes can significantly improve their PEC performance [7]. The ALD process described in the present study is envisaged being a generic technological approach to the fabrication of metal silicide particles (e.g. TiSi, CoSi, NiSi) on Si [1,8,9].

In this study TiSi is fabricated from ALD grown TiO_2 ultra-thin film which is extremely conformal and homogenous. The film is transformed into TiSi by post-annealing which also makes it thermally stable for subsequent film depositions. Our results reveal the initial stages of the island mediated process where the titanium dioxide ultra-thin film undergoes a transformation to suboxides and subsequently to titanium silicide. Furthermore, the laterally resolved chemical composition of the resulting microstructured TiSi surface texture is analyzed.

The phosphorus doped (resistivity 1–20 Ω cm) n-type Si(100) wafers were purchased from Wafer World, Inc. (Florida, USA). The 400 μm thick, three inch diameter pre-polished wafers had been cut in (100) orientation with $\pm 1°$ accuracy. For the experiments 10 × 10 mm^2 squares were cleaved. The details of the annealing and hydrogen plasma based in situ cleaning of the silicon substrates are described in the Supplementary Material. The cleaned silicon substrates were transferred ex situ to Picosun Sunale ALD R200 Advanced reactor for titanium oxide deposition. The air exposure during the sample transfer was kept as short as possible, approximately 5 min.

ALD of titanium dioxide was carried out at a substrate temperature of 200 °C. Deposition consisted of 804 cycles of tetrakis(dimethylamido)titanium(IV) (TDMAT) and deionized water leading to a film thickness of 28.7 ± 0.3 nm as verified

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by ellipsometry (see Supplementary Material). After the deposition the samples were cooled down in N_2 atmosphere before transferring them back to UHV for high temperature annealing.

Two separate UHV systems with a base pressure below 1×10^{-10} mbar were employed for annealing and subsequent electron spectroscopy experiments. X-ray photoelectron spectroscopy (XPS) and energy filtered photoemission electron microscopy (EF-PEEM) measurements were carried out using NanoESCA (Omicron NanoTechnology GmbH) spectromicroscopy system [10]. Focused monochromatized Al Kα radiation ($h\nu = 1486.5$ eV) was utilized for core level spectroscopy and imaging whereas secondary electron tail cut-off maps for work function determination were measured with non-monochromatized He Iα radiation ($h\nu = 21.22$ eV) using HIS 13 VUV Source (Focus GmbH). The XP spectra were collected using a hemispherical analyzer with energy resolution of 400 meV or 50 meV (for high resolution (HR) XPS). For EF-PEEM measurements the energy resolution of an aberration correcting double hemispherical energy analyzer (IDEA) was set to 800 meV for core level imaging and 50 meV for secondary electron imaging. Lateral resolution for core level images was approximately 500 nm and for He Iα excited secondary electron images approximately 100 nm.

High spatial resolution EF-PEEM measurements were performed with a spectroscopic photoemission and low energy electron microscope (SPELEEM) III (Elmitech GmbH) [11] at the soft X-ray beamline I311 of MAX II storage ring in the MAX IV Laboratory synchrotron radiation (SR) facility (Lund, Sweden) [12]. SPELEEM was utilized in photoelectron emission, low energy electron microscopy (LEEM) and imaging X-ray absorption (XAS) secondary electron yield modes.

In addition to XPS and EF-PEEM studies the surface morphology of the 950 °C annealed island structured sample was studied by scanning electron microscopy (SEM; Zeiss Ultra 55, Carl Zeiss Microscopy GmbH) and atomic force microscopy (AFM; Veeco Dimension 3100 AFM, Veeco Instruments Inc.).

Both NanoESCA and SPELEEM III had a heating assembly in their preparation chambers for heat treatments of the samples. For studies performed in the NanoESCA system the ALD grown TiO_2 was initially annealed at 950 °C for 10 min to form titanium silicide islands. Studying the edge areas of these islands with PEEM revealed details of the reduction process involved in the transformation of titanium (sub)oxides to titanium silicide. Subsequently the sample was annealed to 960 °C for 10 min to reduce the remaining titanium oxide areas to continuous titanium silicide ridge-like microstructure.

SEM images in Fig. 1A–C illustrate the TiSi island structure after the 950 °C annealing. Islands nucleate at seemingly random locations and with inhomogeneous size distribution. The ALD grown TiO_2 film is homogenous, and therefore it is likely that the nucleation has been initiated by small impurity particles or crystal defects in the Si substrate. It is noteworthy that the nucleation does not happen instantaneously but requires 5 min to 10 min at 950 °C temperature. Temperatures of

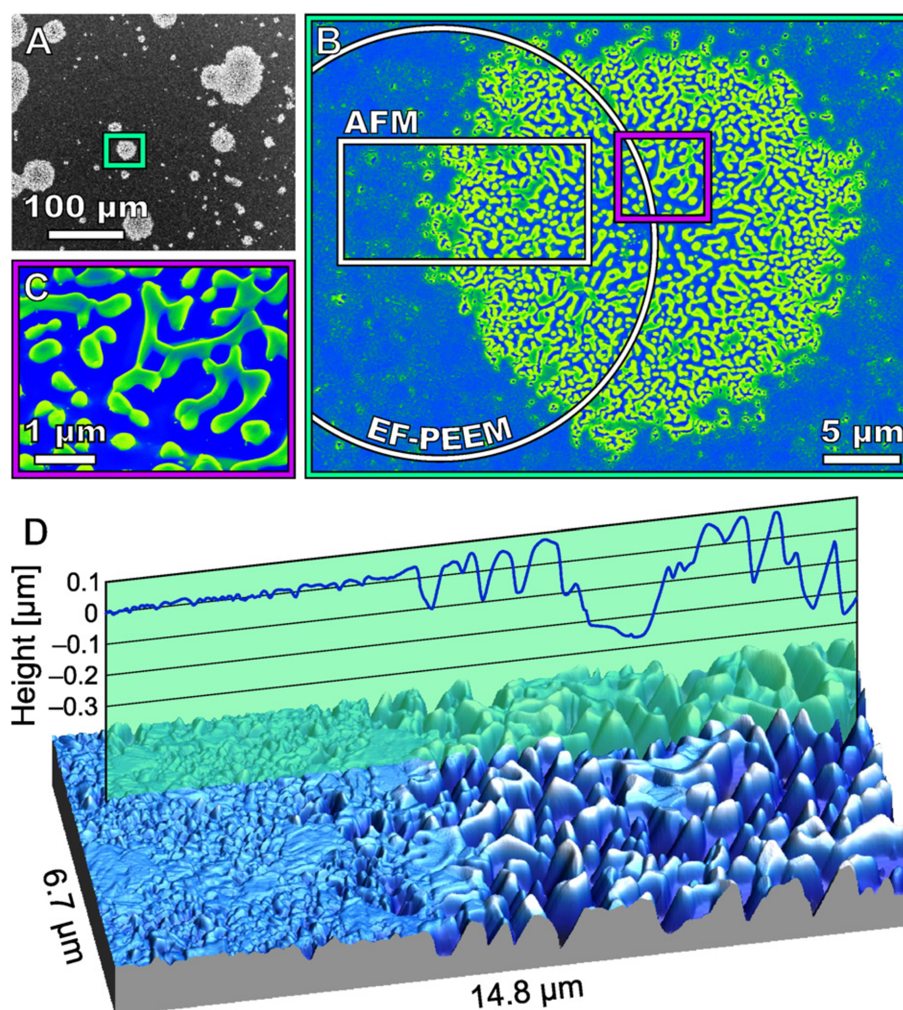

Fig. 1. A–C: SEM images of a highly topographically microstructured TiSi island after 950 °C annealing. Highest magnification in Fig. C shows the detailed TiSi ridge-like microstructure inside the island. The white circle in Fig. B shows the area selected for EF-PEEM studies and will be discussed later in detail. D: AFM image of the region framed with a white rectangle in Fig. B. AFM line profile illustrates the abrupt change in TiO_x surface topography when moving from the area outside the island (left side) to the heavily corrugated ridge-like area inside the island (right side).

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