



# Application of *in situ* chloride-generated route to Ti<sub>5</sub>Si<sub>3</sub> nanowires from and on Si substrate

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## ABSTRACT

Most titanium silicide one-dimensional (1D) nanostructures have been thus far prepared by using titanium chloride as precursor which is very sensitive to air and very inconvenient to the experimental operations. Herein Ti<sub>5</sub>Si<sub>3</sub> nanowires were synthesized on bare Si substrate via *in situ* chloride-generated route, and the shortcomings from the direct use of titanium chloride were well avoided. Furthermore, the Si substrate functions as both Si source and substrate; thus, the synthesis and potential integration of titanium silicide nanostructures on a mature silicon substrate is accomplished by one step. In this way the as-synthesized Ti<sub>5</sub>Si<sub>3</sub> nanowires on Si substrate showed promising field-emission behavior.

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## 1. Introduction

Today the preparations of one-dimensional (1D) transitional metallic silicides become a growing central focus due to their low resistivity, compatibility with conventional silicon manufacturing, and ability to form ohmic contacts to both p- and n-type silicon [1]. Of synthesizing them chemical vapor deposition (CVD) technique is the most intensively used instrument. Since the limitation of delivery of source materials, many easy-delivering precursors such as large organometallic molecules or anhydrous metal chlorides are often preferential [2]. The former are very expensive and virulent [3–5], while the latter quite sensitive to air and strongly corrosive and poisonous [6–14]. Anyway, these easy-delivering precursors are very inconvenient to the experimental operations even regardless of the cost. In our previous report, a convenient *in situ* chloride-generated route was developed to fabricate some advanced semiconducting nanostructures, by which the required chlorides could be *in situ* generated and the shortcomings from the direct use of anhydrous metal chlorides could be well avoided [15,16]. Herein, we continue to apply this route to fabricate titanium silicide nanostructures. Titanium silicide has been widely used in the microelectronics industry primarily because of its metallurgically stable contact to silicon and low resistivity. However most titanium silicide nanostructures have been prepared with TiCl<sub>4</sub> or titanium subchlorides generated from the reaction of TiCl<sub>4</sub> and Ti powder as precursors hitherto [10–14,17]. It is known that titanium chloride is very sensitive to air and very inconvenient to the

experimental operations. Herein by pre-loading NiCl<sub>2</sub>·6H<sub>2</sub>O species into titanium powder with acetone, titanium chloride could be *in situ* generated at elevated temperature via solid-state metathesis (SSM) reaction [18], and the shortcomings from the direct use of titanium chlorides could be well avoided.

Recently, the synthesis and assembly of certain nanostructure directly on conductive substrates have attracted much interest, in which the conductive substrates acted as the roles of both reactants and depositing substrates [19,20]. In this contribution, the Si substrate functions as both Si source and substrate for the growth of 1D titanium silicide nanostructures; thus the synthesis and potential integration of titanium silicide nanostructures on a mature silicon substrate is accomplished in one step. The finally acquired titanium silicide nanowires showed good field-emission properties similar to the report by Lee et al. to a large extent due to the entire contact [12].

## 2. Experimental methods

The detailed experimental procedure was similar to our previous report [15]. Briefly, 0.5 g of solid mixture of Ti powders loaded with 2 mL of NiCl<sub>2</sub>·6H<sub>2</sub>O acetone solution (0.2 mol/L) was put into an alumina boat. Si substrate was put downstream about 10 cm apart from the solid mixture in the alumina boat which was located beforehand into the center of a horizontal quartz tube. The system was first flushed with Ar to remove oxygen and moisture, then heated in Ar with the flowing rate of 100 sccm to 800 °C at the rate of 8 °C/min and kept there for 40 min, finally cooled down to ambient temperature in Ar. The products were characterized by X-ray diffraction (XRD; Philips X'pert Pro diffractometer), scanning electron microscopy

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(SEM; JEOL JSM-6300) equipped with an energy-dispersive X-ray analysis (EDX), and (high-resolution) transmission electron microscopy (TEM; JEOL-JEM-1005, HRTEM; JEM-40001X) equipped with an EDX. The field electron emission measurement was performed by using a parallel-plate configuration in a vacuum chamber at a pressure of  $1 \times 10^{-4}$  Pa, and the cathode–anode distance was regulated by a micrometer with the accuracy of 0.2 mm.

### 3. Results and discussion

The products on the Si substrate were characterized by SEM, EDX and XRD, and the results were shown in Fig. 1. Sparse nanowires were observed with several micrometers in length and several decade nanometers in diameter on the Si substrate (Fig. 1a, b), under which some particle films were also exposed. High magnification SEM image reveals no existence of catalyst particles on the tip of nanowires. The component of products including nanowires and particle films was confirmed by EDX curve in which Si and Ti elements were revealed, suggesting the nanowires and particle films may be composed of Ti–Si-containing binary compound (Fig. 1c). XRD could be contributed to confirm the certain structure of the products. In Fig. 1d, all the diffraction peaks can be indexed to the orthorhombic C54-TiSi<sub>2</sub> phase (JCPDS 710187). However, the EDX pattern shows Si : Ti = 58.6 : 41.4  $\approx$  1.4, suggesting the Si/Ti atomic proportion for the product on bare Si substrate is lower than the theoretic proportion value of 2 in TiSi<sub>2</sub>. Due to the magnified location reflection of as-synthesized product from EDX, the Si signal should come from the product regardless of the existence of Si diffraction peak in XRD pattern. Hence in the product there is other titanium silicide in which Si/Ti atomic proportion is lower than 1. Furthermore, compared with the amounts of TiSi<sub>2</sub>, its amounts are so small that its component cannot be detected by XRD (Fig. 1d). Anyway, the accurate structure of the sparse nanowires on the particle films might not be well and truly reflected by XRD and should be further examined by other instruments such as (HR)TEM analysis.

Low magnification image (Fig. 2a) shows the straight nanowires having length of ca. 5  $\mu$ m and diameters of 50–100 nm, and having no catalyst particles on both ends. High magnification TEM image

(Fig. 2b) from the black square (Fig. 2a) shows the typical smooth nanowire with diameter of 60 nm. A selected-area electron diffraction (SAED) pattern (Fig. 2c) of Fig. 2b indicates a dot pattern, which could be well assigned to (002) and (200) planes of single crystalline hexagonal Ti<sub>5</sub>Si<sub>3</sub> with a preferential growth along [002] zone axis. High-resolution image (Fig. 2d) from the selected section in Fig. 2a and corresponding Fourier transform (inset) clearly indicate the d spacing values of 0.25 nm and 0.33 nm could be well indexed to the (002) and (200) lattice planes of the hexagonal Ti<sub>5</sub>Si<sub>3</sub> phase. The EDX analysis (the low right inset) from the HRTEM indicates the Si/Ti atomic ratio is 36.8:63.2, approaching the ideal value of 0.6 for the theoretically Si/Ti atomic ratio in Ti<sub>5</sub>Si<sub>3</sub>. The microstructure characterizations revealed the component of as-prepared nanowires is Ti<sub>5</sub>Si<sub>3</sub>, though XRD pattern reflected the total product on Si substrate is TiSi<sub>2</sub>.

Herein the reaction temperature, time, and the distance between the Si substrate and the reactant-containing alumina boat played important roles in the controllable synthesis of the Ti<sub>5</sub>Si<sub>3</sub> nanowires. When the reaction temperature was much lower or higher than 800 °C, tiny TiSi<sub>2</sub> particle films or agglomerates were obtained, respectively. The distance between the Si substrate and the reactant-containing alumina boat played similar role to the reaction temperature. Besides the reaction temperature and the reaction distance, the reaction time was also an essential factor for controlling the growth of the single crystalline Ti<sub>5</sub>Si<sub>3</sub> nanowires. When heating the reaction system to 800 °C with similar reaction procedure and cooling down to ambient temperature at once, only TiSi<sub>2</sub> particle films (Fig. 3) could be observed on the Si substrate. This sharp contrast illustrated that, during the temperature-rising stage in Ar, the TiCl<sub>x</sub>(g) species *in situ* generated from the SSM reaction between NiCl<sub>2</sub>(s) and Ti powder would react with Si substrate to form Si-rich TiSi<sub>2</sub> particle films. Once the TiSi<sub>2</sub> particle films were formed, the supply of Si atoms from the substrate would be hampered by the relative inertness of the as-formed TiSi<sub>2</sub> films, thus becoming deficient, and then result in the formation of Ti-rich titanium silicides, i.e. Ti<sub>5</sub>Si<sub>3</sub>. As suggested by Lee et al., Ti<sub>5</sub>Si<sub>3</sub> should be the first silicide phase solidified due to its highest melting point and the lowest standard heat of formation among all of the titanium silicide phases [12].

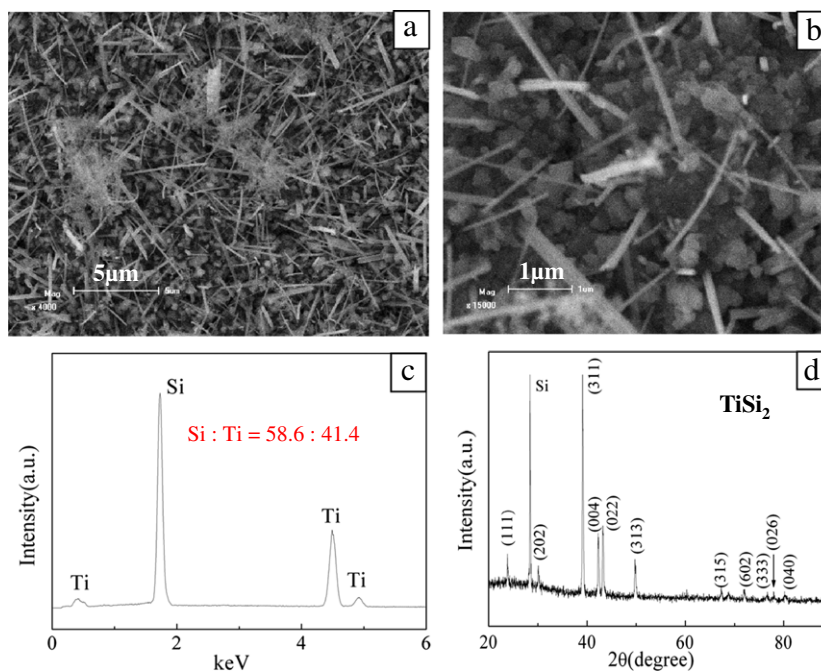


Fig. 1. SEM images (a, b), (c) EDX curve and (d) XRD pattern of the products on Si obtained.

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