

## A Co-reduction–Silicification Route to $\delta$ -Ni<sub>2</sub>Si Nanowire

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$\delta$ -Ni<sub>2</sub>Si nanowires have been synthesized via a co-reduction–silicification route, using anhydrous NiCl<sub>2</sub> and SiCl<sub>4</sub> as nickel source and silicon source, respectively, and metallic Na as reductant in an autoclave at 600 °C for 16 h. Transmission electron microscopy (TEM) observations show that the diameters of nanowires ranged in 10–100 nm and lengths up to several tens micrometers. The possible formation mechanism is discussed.

Owing to the unique range of properties as high melting point, low density, low electrical resistivity and high resistance to oxidation and corrosion, transition metal silicides have been identified as highly promising candidates for diverse fields of application including high temperature heating materials, interface diffusion barriers and in large scale integrated (ULSI) circuit technology.<sup>1–3</sup> Among them, nickel silicides are one of the most widely studied silicide systems due to their high temperature performance and microelectronics application, and have been demonstrated as one of the most promising silicide materials for future ULSI, thin film transistor (TFT), and novel devices.<sup>1,4</sup>

Generally, transition metal silicides are prepared by either direct element reaction,<sup>5</sup> co-reduction of SiO<sub>2</sub> with aluminium or carbon,<sup>6</sup> self-propagating high-temperature synthesis,<sup>7</sup> solid-state metathesis<sup>2</sup> at elevated temperatures, or various powder techniques.<sup>8</sup> Previously, we have developed a co-reduction method to synthesize nanocrystalline silicides (carbides) by allowing SiCl<sub>4</sub> (CCl<sub>4</sub>) and MCl<sub>4</sub> to react with metallic sodium at relatively low temperatures.<sup>9,10</sup> Recently, nickel silicide nanowires were synthesized by decomposition of silane on nickel surface, which could be one dimensional transport of carriers on future devices.<sup>11</sup> Herein, we report a co-reduction–silicification route to synthesize  $\delta$ -Ni<sub>2</sub>Si nanowires.

All reagents used in our experiments were analytical pure grade, purchased from Shanghai Chemicals Co. (China). Anhydrous NiCl<sub>2</sub> was obtained by the dehydration of NiCl<sub>2</sub>·6H<sub>2</sub>O with thionyl chloride as dehydrant. All manipulations were carried out in a dry glovebox with N<sub>2</sub> flowing. Typically, 8 mmol of anhydrous NiCl<sub>2</sub> and a little excessive liquid SiCl<sub>4</sub> with excessive granular metal Na were put into a stainless steel autoclave of 50-mL capacity. After the autoclave was sealed, it was maintained at 600 °C for 16 h and then cooled to room temperature. After marinated in absolute alcohol, the precipitate was filtered off and washed with distilled water, diluted HCl and absolute alcohol for several times to remove NaCl and other impurities, and then dried in a vacuum at 60 °C for 4 h, the final black product was obtained.

X-ray powder diffraction (XRD) patterns were recorded on a Japan Rigaku Dmax- $\gamma$ A X-ray diffractometer with graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å). TEM images were taken with a Hitachi Model H-800 transmission

electron microscope. High-resolution electron microscopy (HRTEM) images were obtained with a JEOL-2010 transmission electron microscope.

Figure 1 shows a typical XRD pattern of the prepared samples. All of the sharp and intensive peaks can be indexed to a rhombohedral phase [space group: *Pbnm*(62)] of crystalline  $\delta$ -Ni<sub>2</sub>Si. The calculated cell constants are  $a = 7.066$ ,  $b = 5.011$ ,  $c = 3.726$  Å, in good agreement with the literature (JCPDS 48-1339).

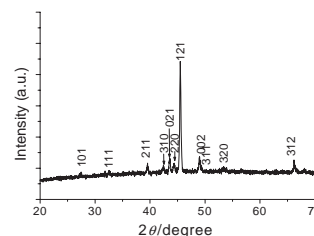


Figure 1. Typical XRD pattern of the  $\delta$ -Ni<sub>2</sub>Si samples.

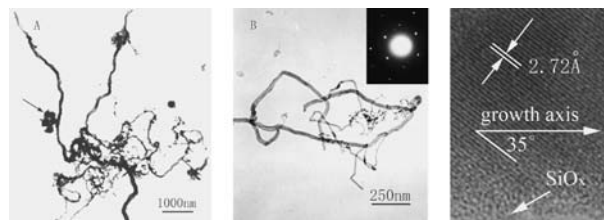
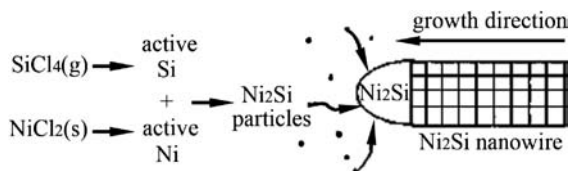


Figure 2. Typical TEM images (A, B) and HRTEM image of the prepared sample.

TEM images of the prepared samples (shown in Figures 2A and 2B) show that a significant amount of the sample dispersed on the TEM copper grids are nanowires, with diameters of 10–100 nm and lengths of up to several tens micrometers, although other irregular particles (marked by the arrow in Figure 2A) also appear. Electron diffraction (ED) pattern (inset in the Figure 2B) obtained from a single nanowire confirms that the prepared nanowire is single crystal. From the HRTEM image of a single nanowire with outer diameter of about 33 nm, we can see that the nanowire has a crystalline core nipped by amorphous layers with atomically sharp interfaces. The clear lattice fringes of the crystalline core, with the fringe spacing (calculated  $2.72$  Å) close to that of (111) lattice planes of bulk  $\delta$ -Ni<sub>2</sub>Si, suggests that the in-plane layers of the nanowire are  $\delta$ -Ni<sub>2</sub>Si (111) facet with a perfect atomic, defect-free, single-crystal structure. The angle between the growth axis direction and the direction parallel to the (111) lattice facet is about 35°. The thickness of the amorphous layers varies from 1 to 3 nm, energy-dispersive X-ray spectrum (EDS) analysis shows that the chemical components

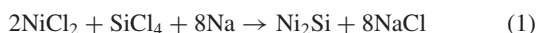


**Figure 3.** The sketch illustrates the formation process of  $\delta$ -Ni<sub>2</sub>Si nanowires.

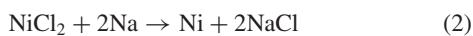
of the amorphous edges of the nanowire is silicon oxide (SiO<sub>x</sub>).

The specific formation mechanism of the  $\delta$ -Ni<sub>2</sub>Si nanowires is not yet clear and warrants further investigation. From the TEM images, we find that there are no nano-sized metal balls at the tips of these nanowires. This observation suggests that the nanowires do not grow by vapor-liquid-solid (VLS)<sup>12</sup> or solution-liquid-solid (SLS)<sup>13</sup> growth mechanisms proposed for nanowires grown by a catalytic technique, in which a liquid metal droplet is located at the tip of the wires and serves as the catalytic active site. W. Z. Wang et al.<sup>14</sup> had used an Ostwald ripening mechanism<sup>15</sup> to explain the formation of Mn<sub>3</sub>O<sub>4</sub> nanowires, in which NaCl was added to decrease the viscosity of the melt and increase the mobility of components in the flux. This strongly induces us to speculate that the growth of  $\delta$ -Ni<sub>2</sub>Si nanowires under our experimental conditions may be much close to Ostwald ripening mechanism. The detail formation process may be illustrated in Figure 3 and described as following.

According to the previous research<sup>9,10,16,17</sup> and our experiment results, we believe that the total reaction for the formation of  $\delta$ -Ni<sub>2</sub>Si in our experimental system may be formulated as follows:



The reaction (1) may include the following reactions:



The above reactions are all thermodynamically spontaneous and exothermic (reaction (2):  $\Delta G_r^\circ = -164.06 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta H_r^\circ = -170.78 \text{ kJ}\cdot\text{mol}^{-1}$ ; reaction (3):  $\Delta G_r^\circ = -919.16 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta H_r^\circ = -987.13 \text{ kJ}\cdot\text{mol}^{-1}$ ; reaction (4):  $\Delta G_r^\circ = -22.9 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta H_r^\circ = -47.7 \text{ kJ}\cdot\text{mol}^{-1}$ ).<sup>18,19</sup> At the beginning of the reactions, the melted metallic Na reduced the reactants NiCl<sub>2</sub> and SiCl<sub>4</sub> to element Ni and Si, respectively, meanwhile released a large quantity of caloric, which might raise the temperature of our reaction system higher enough to melt the vice-product NaCl (melting point 801 °C). The new-formed element Ni and Si may have high reaction activity, and then, the fine particles of  $\delta$ -Ni<sub>2</sub>Si were formed by silicification reaction at high temperature simultaneously. Furthermore, the molten Na and NaCl significantly decreases the viscosity of the system and provides a favorable liquid environment for the mobile of components in the flux, which makes it easier for the fine particles of  $\delta$ -Ni<sub>2</sub>Si to further fabricate nanowires core.

The trace amount of air remnant in the autoclave, which may

oxidize the silicon during the reaction process, may be responsible for the formation of the silicon oxide (SiO<sub>x</sub>) amorphous layers. Moreover, the formation of the wrapping silicon oxide (SiO<sub>x</sub>) amorphous layers may retard the lateral growth of  $\delta$ -Ni<sub>2</sub>Si, which may favorite for the growth of  $\delta$ -Ni<sub>2</sub>Si nanowires.

In summary, a co-reduction-silicification route, by using anhydrous NiCl<sub>2</sub>, SiCl<sub>4</sub> and metallic Na as nickel source, silicon source and reductant, respectively, has been applied to synthesize single-crystal  $\delta$ -Ni<sub>2</sub>Si nanowires with diameters of 10–100 nm and lengths up to several tens micrometers. And the possible formation process of the nanowires is discussed.

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