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Low-temperature synthesis of Si nanowires using multizone chemical vapor deposition methods

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With a multitemperature zone chemical vapor deposition reactor, silicon nanowires (SiNWs) were synthesized at temperatures below the Au–Si eutectic point, with Au nanoparticles as the growth seeds. Nanoparticle seeds with diameters less than 60 nm were used to grow NWs at temperatures below 350 °C. A strong dependence on the growth rate with the synthesis temperature and the size of the Au nanoparticle seeds was observed. With 10 nm particles, SiNWs were reproducibly synthesized at a temperature of 290 °C. We suggest that the governing role for the synthesis lies in the diffusion of Si feeding into the growth seeds. © *2008 American Institute of Physics*.
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As promising building blocks for the next generation's nanometer-scale electronic, mechanical, and optical devices, silicon nanowires (SiNWs) have attracted intensive research efforts.[1] Various methods have been developed to synthesize SiNWs, among which chemical vapor deposition (CVD) offers advantages such as excellent control over quantity, quality, diameter, and length of the nanowires.[1–5] Existing SiNW CVD growth, however, usually requires temperatures above 400 °C, depending on the gas precursors and growth seed materials used.

Direct deposition of SiNWs onto low-melting point substrates, e.g., plastic or glass, would allow the direct integration of these disparate materials for applications in flexible or transparent electronics. The use of transfer techniques for integrating NWs from their growth substrate onto a different platform has shown promise[6] but the additional transfer steps increase the complexity of the process. The device performance of SiNW field-effect transistors (FETs) have been shown to be comparable to its conventional Si FET counterparts[7] and low-temperature synthesis of these materials could potentially enable direct integration of high-performance electronic devices on flexible platforms.

Successful SiNW synthesis is often explained by the vapor-liquid-solid[8,9] (VLS) or vapor-solid-solid (VSS) mechanism,[10] which impose two thermodynamic constraints on the lowest growth temperature that can be achieved: precursor decomposition for creating available source material and diffusion into the growth seed for deposition. The former is determined by the chemical stabilities, and the latter is dictated by the intrinsic properties of the Si-seed system, both are sensitive to temperature. Existing low-temperature growths (<400 °C) represent efforts to separate the two processes. Solution-phase synthesis, for example, provides sufficient and fast feeding at relatively low temperatures;[11,12] alternatively, plasma has been utilized to decompose precursors (SiH_4 or $SiCl_4$) at temperatures where spontaneous decomposition does not occur.[13] In this letter, we demonstrate the synthesis of SiNWs at temperatures as low as 290 °C using a multitemperature zone furnace. The low-temperature synthesis is enabled by the independent control over the precursor feeding and the nanowire growth, leading to a balanced VLS or VSS growth system.

A three-temperature-zone furnace reactor (manufactured by Atomate Corporation) was used for the NW synthesis and is schematically illustrated in Fig. 1. For a typical growth, the chamber pressure was set to 100 Torr and the temperature of zone 1 (T_1) was set to 450 °C to decompose the SiH_4 precursor. The temperature of zone 2 (T_2) was chosen between 350 and 400 °C as a transition region and the tem-

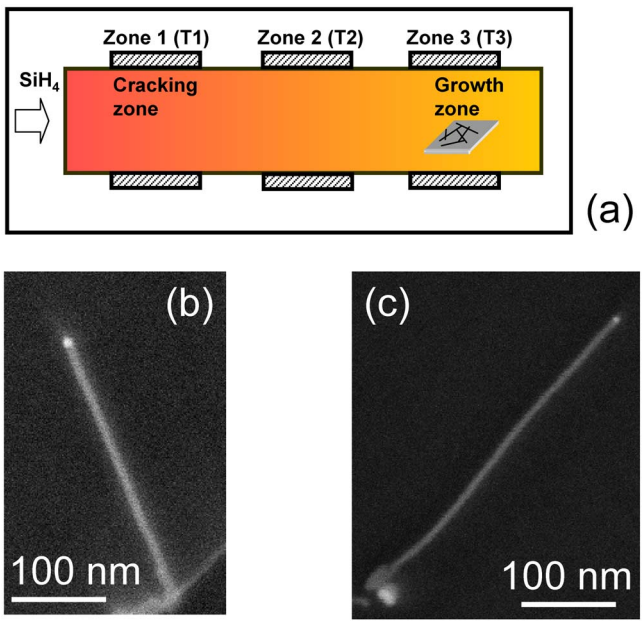

FIG. 1. (Color online) (a) Schematic drawing of the three-zone furnace for the low-temperature Si nanowire growth. Zone 1, the "cracking zone" is set at T_1=450 °C to decompose the precursor SiH_4 with H_2 as the carrier gas. The SiNW synthesis, using a Si substrate with Au NP seeds, is located in zone 3 with the growth temperature $T_3 < T_1$. [(b) and (c)] Typical scanning electron microscope (SEM) images of Si nanowires grown at 290 °C. Au NP can be seen at the tip of SiNWs and the wires are uniform in diameter.

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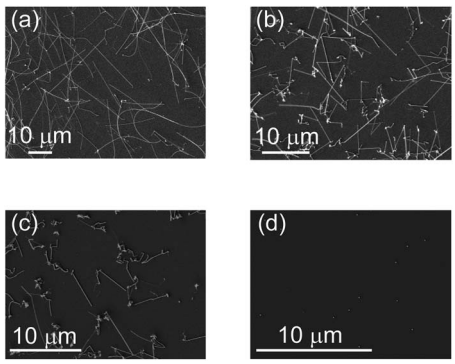

FIG. 2. SEM images of SiNWs grown from ~60 nm diameter Au colloids at various growth-zone temperatures (T_3). (a) At 400 °C, long SiNWs (>20 μm) were obtained; at (b) 375 °C and (c) 350 °C, shorter and occasionally defective SiNWs were observed, and (d) no SiNW growth was observed at 320 °C.

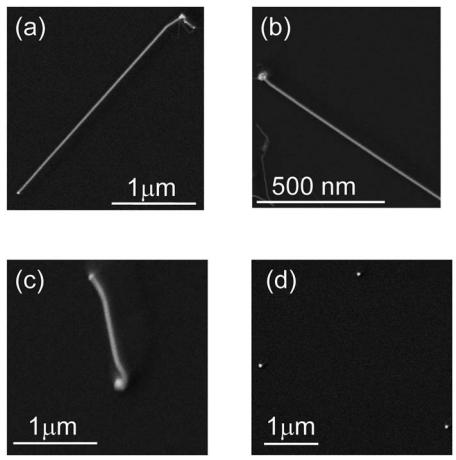

FIG. 3. Au catalyst size dependence for SiNW growth at 320 °C (T_3). With all other growth parameters constant, Au growth seeds were varied from 10 to 40 nm. The average lengths of the as-grown SiNWs were 3, 2, and 1 μm for (a) 10 nm, (b) 20 nm, and (c) 40 nm Au seeds, respectively. (d) For 60 nm Au seeds, no wires were observed due to the complete suppression of growth. A nanowire length variation of ±10% was measured.

perature of zone 3 ($T_3 < T_1$ or T_2) was set to the growth temperature. Each temperature zone was independently measured and controlled. The separation between the high-temperature zone and the growth zone was at least 20 cm, permitting isolation of the high temperatures needed for SiH_4 decomposition and the low temperatures that are sufficient to sustain reactive Si species for the subsequent SiNW growth. H_2 was used as the carrier gas.

The effect of the growth-zone temperature on NW growth rate was first studied. T_3 was varied between 320 and 400 °C using commercially available 60 nm Au catalysts (Fig. 2). At T_3=400 °C, SiNWs ~20 μm long were achieved after 30 min of growth [Fig. 2(a)]. Lowering the temperature to 375 °C led to shorter SiNWs (<15 μm) occasionally with defects [e.g., kinks, Fig. 2(b)]. Further decreasing the growth temperature to 350 °C resulted in even shorter SiNWs (<5 μm), with noticeably reduced yield and more defects [Fig. 2(c)]. When T_3 was set to 320 °C, the growth was completely suppressed [Fig. 2(d)].

While SiNWs failed to grow from 60 nm Au growth seeds at T_3=320 °C, smaller diameter NWs were successfully obtained at the lower temperatures. In another set of experiments, we carried out the growth at T_3=320 °C using commercially available Au seeds varying from 10 to 40 nm in diameter. The average lengths of the as-grown SiNWs were 3, 2, and 1 μm for 10, 20, and 40 nm Au seed, respectively (Fig. 3). In addition, we found that growth from the larger seeds (e.g., 40 nm) was present with more defects at the low growth temperature, suggesting the smaller diameter SiNWs have a reduced kinetic barrier for growth at the lower temperatures. To elucidate the details of the low-temperature growth, we next focused on 10 nm growth seeds and systematically varied the reaction temperature (T_3). With this approach, the lowest temperature at which pristine SiNWs were obtained was at 290 °C [Figs. 1(b) and 1(c)].

Nanometer-scale particles are known to exhibit lower melting points than their bulk counterparts, with Au particles down to 5 nm exhibiting a relative lowering by ~20%.[14,15] In this study the smallest Au particles, with a 10 nm diameter, would only exhibit a melting point reduction of ~8% and formation of a liquid surface layer is not expected.[15] We therefore suggest that formation of a Si–Au liquid alloy is not involved in the growth under these low temperatures. Instead, Si atoms diffuse along the surface or through the solid Au NPs,[10,16,17] similar to recent reports on the Ge–Au system under comparably low temperatures.[18] That is, the growth mechanism for the low-temperature synthesis is VSS, compared with VLS at higher temperatures (>340 °C for 10 nm SiNWs). In the absence of Au nanoparticles (NPs), nanowire growth was not observed.

The VSS growth mechanism is the direct result of the fast feeding of reactive Si species due to an efficient SiH_4 decomposition region (450 °C at 100 Torr) and an isolated low-growth temperature region, much lower than that needed for liquid alloy formation. Once reaching the growth site, Si atoms diffuse through the solid Au NP seeds to deposit and crystallize on the Au–Si interface, yielding SiNWs. The solid-state process is typified by a lower diffusion coefficient, hence lower kinetics. It is also more sensitive to the diffusion length—longer paths are often exceedingly difficult to sustain a balanced diffusion rate to match that of the feeding and crystallization, resulting in growth failure. In our experiments, larger Au NPs, e.g., 60 nm, did not result in SiNWs growth at low temperatures. Similar to Ref. 10, we argue that the key driving force of the low-temperature growth is the high concentration of Si feeding ($C_{\text{Si-}g}$).

We also observed a clear transition in the growth kinetics for 10 nm SiNWs at ~340 °C, above which the growth rate is more sensitive to temperature. We suggest this transition manifests the transition of VLS to VSS as the temperature is reduced (Fig. 4). It is a reasonable hypothesis considering the size of the catalysts particles and the kinetics of the nanowire synthesis. First, the melting point reduction as a function of particle size is relatively insignificant for particles larger than 5 nm. The 340 °C transition temperature suggests that the eutectic temperature of 10 nm Au–Si system is about 20 °C lower than the bulk, a figure that is consistent with the literature.[14] Second, we consider the quantitative descriptions of the SiNW growth kinetics. It may be expressed as $(dL/dt)=(J_D/\rho r)$, where ρ is the Si atomic density and r the radius of the growth seed; $J_D=D\Delta C_{\text{Si}}$ is the net influx of Si. In turn, $D=D_0 \exp(-E_a/k_BT)$ is the diffusion coefficient. Thus we arrive at

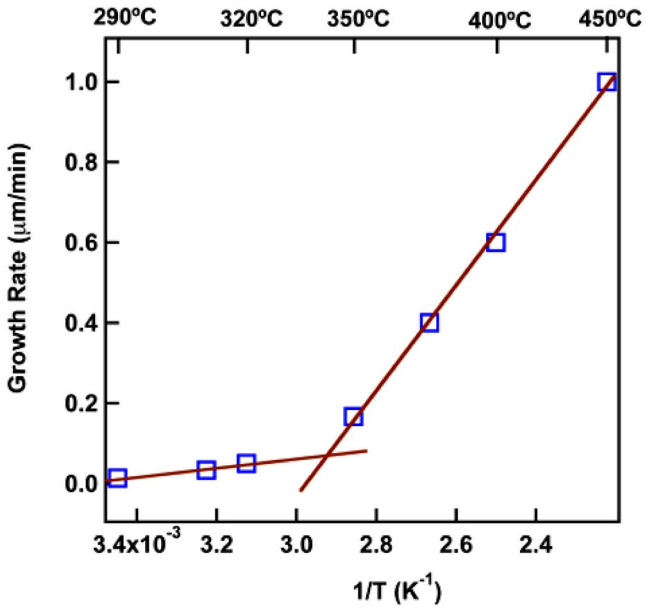

FIG. 4. (Color online) Temperature dependence of SiNW growth rates from 10 nm Au nanocolloids. T_3 was varied from 290 to 450 °C for 30 min of growth while all other growth parameters were constant. A transition point at ~340 °C was observed, indicating the growth mechanism switched from VLS to VSS.

$$\frac{dL}{dt} = \frac{D_0 \exp\left(-\frac{E_a}{k_B T}\right)\Delta C}{\rho r}. \quad (1)$$

This result implies that for the same size growth seeds (e.g., a diameter of 10 nm), and the same feeding (T_1 is fixed for all experiments described in this letter), the growth rate is only influenced by the diffusion coefficient of Si in Au or the Au–Si alloy. The observed transition point of the growth kinetics at 340 °C thus supports the hypothesis of a diffusion medium change,[19] a transition from VLS to VSS (Fig. 4). It should also be noted that for the temperature range limits, more quantitative analysis and research is needed to fully reveal the details, but the results shed light on the significance of separating the precursor feeding from the nanowire growth for low-temperature nanowire synthesis.

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