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Morphology of germanium nanowires grown in presence of B₂H₆

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We study the Au-catalyzed chemical vapor growth of germanium (Ge) nanowires in the presence of di-borane (B_2H_6), serving as doping precursor. Our experiments reveal that, while undoped Ge nanowires can be grown epitaxially on Si(111) substrates with very long wire lengths, the B_2H_6 exposure renders the Ge nanowires significantly tapered. As we describe here, this peculiar morphology stems from the combination of the acicular, one-dimensional nanowire growth and a dramatically enhanced, B-induced conformal Ge deposition. The combination of acicular and conformal Ge growth mechanisms results in cone-shaped Ge nanostructures. © 2006 American Institute of Physics. [DOI: 10.1063/1.2165089]

There has been significant interest lately in the metalcatalyzed growth of semiconductor nanowires. Experimentally, group IV semiconductors Si¹ and Ge,² as well as III-V compounds, e.g., InAs, InP,³ GaAs,⁴ have been shown to exhibit metal catalyzed, one-dimensional crystal growth. The interest in these structures is fuelled in part by the promise of novel devices, relevant to complementary metal-oxidesemiconductor (CMOS) technology scaling.⁵ Among semiconductor nanowire systems expected to be compatible with silicon technology, germanium is of particular interest, stimulated by the prospect of replacing Si as a semiconducting channel in MOS field effect transistors, due to its higher carrier mobilities. Several groups have recently reported Aucatalyzed, chemical vapor growth of Ge nanowires.^{2,6} A potential advantage of semiconductor nanowires is that electronic doping in these devices should be a straightforward extension of semiconductor bulk doping. Therefore, the study of nanowire growth in presence of dopants, as well as dopant incorporation during growth, is of importance to nanowire device design.

Here we examine the low-temperature, chemical vapor growth of Au-catalyzed Ge nanowires in the presence of diborane B_2H_6 , serving as our doping precursor. Our experiments reveal that B_2H_6 dramatically enhances the conformal deposition of Ge at low temperatures, enhancing lateral growth rates and thereby resulting in cone-like and not rodlike nanostructures. These findings impose constraints on modulating the Ge nanowire doping *along* the wire length during the growth, but open the tantalizing possibility of using the low-temperature, highly B-doped Ge layers in conjunction with a dielectric as gate/dielectric stack for Ge nanowire transistors.

In Fig. 1(a) we show one example of Ge nanowires epitaxially grown on a Si substrate. Prior to loading into the chemical vapor deposition (CVD) reactor, a 10Å-thick Au film was deposited on the H-terminated Si(111) substrate. The substrate was annealed *in situ* at a temperature T= 500 °C in an atmosphere of H₂ in order for the Au film to form droplets, followed by a cool-down to the optimal, T= 285 °C growth temperature. The 2 h long nanowire growth was done at a total pressure of 5 Torr, using a 60 sccm flow of GeH₄ (10% in a helium mixture). Under these conditions the wires grow at an average rate of 4 μ m/h (Ref. 7) and with diameters ranging from 20 to 50 nm. The onedimensional, nanowire crystal growth is generally attributed to the vapor-liquid-solid phase mechanism.⁸ In this model the metal catalyst and the semiconductor form an eutectic alloy. At temperatures higher than the eutectic temperature, the catalyst becomes liquid and facilitates the transport of semiconductor atoms from the vapor ambient to the crystal. In our experiments, the Ge nanowires distinguish themselves because they grow at temperatures significantly lower the Au–Ge eutectic temperature (360 °C), therefore the Au catalyst remains in the solid phase.

The noteworthy feature of Fig. 1(a) is that the Ge nanowires align with the [111] directions of the Si substrate: they



FIG. 1. (Color online) (a) Scanning electron micrograph (SEM) showing Ge nanowires epitaxially grown on a Si(111) substrate. The wires grow mainly along the different [111] crystal directions, indicated by arrows in the figure. (b) X-ray diffraction *k*-space mapping of the Ge nanowires grown on Si.

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FIG. 2. Top-down (a) and cross-section (b) SEM view of Ge nanowires grown in presence of B2H6. The Ge nanowires are markedly different than those grown without B₂H₆. The cone dimensions agree well with estimates based on the B-enhanced Ge planar deposition rate.

can grow either normal to the substrate, or along the other three crystallographic [111] directions which form 70.5° angles with the normal.

To further substantiate the findings of Fig. 1(a) we have performed an x-ray diffraction k-space mapping of the Ge nanowires on Si(111) samples. The experiments were done by measuring a series of x-ray rocking curves around the Si(111) diffraction peak, at various incidence angles between the x-ray beam and the substrate. The data is presented in Fig 1(b). Here, ω denotes the angle between the incident x-ray beam and the substrate and 2θ is the angle formed by the directions of the incident and reflected x-ray beams. These data show clearly the Si(111) and Ge(111) diffraction peaks, corresponding to the fully relaxed Si and Ge lattice constants. The data bear similarities with x-ray rocking curves from planar germanium on insulator substrates.⁹ The vertical, $\pm 2^{\circ}$ extension of the Ge(111) peak along the ω axis indicates that Ge nanowires axis' can slightly deviate from the [111] directions of the substrate. The Ge(111) diffraction peak full width at half maximum along the $\omega/2\theta$ direction is 0.12°.

In Fig. 2 we show an example of Ge nanowires on Si substrates grown in the presence of B_2H_6 . The substrate preparation and growth conditions are identical with those used for the sample of Fig. 1, with the only difference that during the growth we introduced a small, 2 sccm, flow of 1%-diluted B_2H_6 . As it can be readily seen from the images of Fig. 2, the Ge nanowires are rendered conical with a typical cone base diameter of 400 nm. Further experiments show that the Ge cone growth and dimensions depends little on temperature in the 255-320 °C range, except for the "cone" density which increases at higher temperatures.

As we show here, this unusual growth morphology results from the combination of the acicular, one-dimensional nanowire growth and the conformal, B-enhanced Ge deposition, which results in two-dimensional lateral growth. B-dependence Ge CVD growth rates data at low temperatures are scarce in the literature. In order to test the conformal Ge deposition enhancement in presence of boron, we have carried out a growth at normal nanowire growth conditions, but using a *bare* Si substrate, without the Au catalysts. Our experiments show that at T=285 °C, 60 sccm GeH₄ (10%) flow, 2 sccm B_2H_6 (1%) flow, and total pressure 5 Torr, the B-doped germanium deposits at a rate of 2.7 nm/min. Note that the normal CVD growth of Ge at such low temperatures is otherwise not possible. The pres-



FIG. 3. (a) SEM view of regular, undoped Ge nanowires. (b) Ge nanowires grown initially without B₂H₆ followed by a second growth stage during which both GeH4 and B2H6 are present in the CVD chamber. Both growths were performed at 285 °C. Note that the second growth of (b) yields a conformal 160-180nm-thick shell which wraps around the undoped Ge core, resulting in 400-nm-thick rods.

ence of an electronic dopant such as diborane clearly catalyzes and enhances the Ge CVD growth process, a phenomenon long known for the case of Si CVD.¹⁰

The B-enhanced Ge two-dimensional deposition translates into a nanowire radius increase during growth. If R_v and R_l are the vertical and lateral growth rates, respectively, then the diameter [d(y)] of a wire as a function of distance from the base at time t is given by

$$d(y) = 2(t - y/R_v)R_l + d_0,$$
(1)

where d_0 is the initial diameter of the wire determined by the seed. The radius change is proportional to the exposure time, the net result being a cone rather than a constant radius nanowire. For a 2.7 nm/min Ge planar growth rate, a nanowire which starts out at 20 nm, will see an increase of 160 nm of its radius during a 1 h growth. The cone geometry of Fig. 2, which is representative of our results for Ge wire grown in the presence of B₂H₆, corresponds to a ratio $R_v/R_l \cong 13$. Corroborated with our lateral growth rate $R_l = 160 \text{ nm/h}$, we obtain a vertical growth rate of $R_{\nu}=2 \ \mu m/h$ for Ge nanowires grown in the presence of B₂H₆. This rate is in good agreement, albeit slightly lower than the typical 2–4 μ m/h growth rate of undoped Ge nanowires of Fig. 1. As a comparison, R_v/R_l for undoped wires is ≥ 500 .

To further demonstrate the effect of B-enhanced Ge deposition we have carried out a 1 h, undoped Ge nanowire growth, followed by a 1 h growth during which both GeH₄ and B_2H_6 were introduced in the CVD chamber. The results are shown in Fig. 3. Panel (a) of Fig. 3 shows the result of a regular, 1 h undoped Ge nanowire growth from Au film catalyst, which exhibits typical Ge nanowires of 20 nm diameter. In panel (b) we show the result of a regular nanowire growth followed by a 1 h growth during which both GeH_4 and B_2H_6 were used. Growth conditions for the latter were the same as except for the presence of boron: 60 sccm GeH₄ (10%), 2 sccm B_2H_6 (1%), T=285 °C, 5 Torr. The data of Fig. 3(b) clearly show that the second stage growth simply results in coating the undoped Ge nanowires with a shell of B-doped germanium. The 400 nm diameter of this core/shell structure is consistent with the 2.7 nm/min planar Ge deposition rate in the presence of boron.

Next we address the question of boron incorporation in the Ge shells. To quantify this, we have grown a core/shell

structure similar to that of Fig. 3(b), except that the shell thickness was 12 nm thick. The nanowires were dispersed on a highly conductive Si substrate with a 30nm-thick thermally grown oxide. Using standard electron-beam lithography followed by lift-off we patterned Ni leads in order to contact the nanowires. Our measurements show that B-doped Ge nanowires exhibit resistor-like I-V characteristics and show very little change to a voltage applied to Si substrate, which acts as a backgate here. Since undoped Ge nanowires are insulating in the same transport configuration, we conclude that the transport in the B-doped Ge nanowire occurs in the B-doped shell. In order to quantify the dopant concentration in the B-doped Ge shells, we have scaled the measured resistance of the B-doped Ge nanowires by the wire length as well as by the shell cross-section area, in order to measure the shell resistivity. The result is $\rho = 0.001 - 0.004 \ \Omega$ cm. These numbers correspond to a carrier concentration of 0.7-4 $\times 10^{19}$ cm⁻³ for the B-doped Ge shell.¹¹

The B-enhanced, highly doped Ge conformal growth shown in Fig. 3 opens up the tantalizing possibility of a low temperature, Ge nanowire based, cylindrical metal-oxidesemiconductor field effect transistor growth. For example, in the first stage an undoped Ge nanowire growth is used to create the Ge core which serves as the transistor's channel. Next, a low temperature conformal dielectric growth, e.g., atomic layer depositions of Al_2O_3 , followed by a highly B-doped Ge shell, will create the dielectric and the gate, respectively. The undoped wire acts a the semiconducting channel, while the highly doped Ge shell acts as gate, much like the highly doped, polycrystalline Si gates used in current CMOS technology.

Finally, we comment on the role of B_2H_6 concentration in enhancing the conformal Ge deposition at low temperature and the ensuing nanowire tapering. Our experiments were focused on a relatively high, 1% concentration of the B_2H_6 precursor. To explore the effect of B_2H_6 dilution, we have performed a similar growth to that of Fig. 2 except for a lower B_2H_6 concentration: namely T=285 °C, 60 sccm GeH₄ (10%), 2 sccm B_2H_6 (20 ppm), and total pressure 5 Torr. In these conditions, our results show conformal Ge deposition of about 20 nm/h, and Ge nanowire tapering corresponding to a ratio $R_v/R_l \approx 180$. While this ratio still indicates a significant wire tapering compared to the undoped case, the lower B₂H₆ dilution clearly results in less of a nanowire tapering.

In summary we have presented an unusual growth mechanism of Ge nanowires exposed to B_2H_6 , which results in a highly doped shell growth, and also quantified the B incorporation in the Ge shell. Our study point out that the doping of Ge nanowires may not be straightforward, and substantially complicate attempts to modulate the doping profile *along* the wire. On the other hand, these findings open-up possibilities of a low temperature core/dielectric/ gate *in situ* field effect transistor growth.

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- ¹Y. Cui and C. M. Lieber, Science **291**, 851 (2001); M. K. Sunkara, S. Sharma, R. Miranda, G. Lian, and E. C. Dickey, Appl. Phys. Lett. **79**, 1546 (2001).
- ²Y. Wu and P. Yang, J. Am. Chem. Soc. **123**, 3165 (2001); D. Wang and H. Dai, Angew. Chem., Int. Ed. **41**, 4783 (2002).
- ³M. T. Bjork, B. J. Ohlsson, T. Sass, A. I. Persson, C. Thelander, M. H. Magnusson, K. Deppert, L. R. Wallenberg, and L. Samuelson, Appl. Phys. Lett. **80**, 1058 (2002).
- ⁴B. J. Ohlsson, M. T. Björk, M. H. Magnusson, K. Deppert, L. Samuelson, and L. R. Wallenberg, Appl. Phys. Lett. **79**, 3335 (2001).
- ⁵Y. Cui, Z. H. Zong, D. L. Wang, W. U. Wang, and C. M. Lieber, Nano Lett. **3**, 149 (2003).
- ⁶A. B. Greytak, L. J. Lauhon, M. S. Gudiksen, and C. M. Lieber, Appl. Phys. Lett. **84**, 4176 (2004); J. L. Taraci, J. W. Dailey, T. Clement, D. J. Smith, J. Drucker, and S. T. Picraux, *ibid.* **84**, 5302 (2004); T. I. Kamins, X. Li, and R. S. Williams, Nano Lett. **4**, 503 (2004).
- ⁷The nanowire growth rate is independent of the wire diameter. The wire length variation on the sample likely results from variations in growth onset of individual wires.
- ⁸R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
- ⁹N. A. Bojarczuk, M. Copel, S. Guha, V. Narayanan, E. J. Preisler, F. M. Ross, and H. Shang, Appl. Phys. Lett. **83**, 5443 (2003).
- ¹⁰L. H. Hall and K. M. Koliwad, J. Electrochem. Soc. **120**, 1438 (1973); P. Rai-Choudhury and P. L. Hower, *ibid.*, **120**, 1761 (1973).
- ¹¹D. B. Cuttriss, Bell Syst. Tech. J. 40, 509 (1961).