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Composition and growth direction control of epitaxial vapor-liquid-solid-grown SiGe nanowires

Eric Dailey,[1] Prashanth Madras,[1] and Jeff Drucker[1,2,a)]
[1]*School of Mechanical, Aerospace, Chemical and Materials Engineering, Arizona State University, Tempe, Arizona 85287-6106, USA*
[2]*Department of Physics, Arizona State University, Tempe, Arizona 85287-1504, USA*

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The composition and growth direction of epitaxial SiGe alloy nanowires (NWs) grown via the Au-catalyzed vapor-liquid-solid technique can be controlled by varying growth conditions. These alloy NWs can adopt either Si-like or Ge-like characteristics. Si-like growth is characterized by Au-coated ⟨111⟩-oriented NWs for low pressure growth and Au-free ⟨112⟩-oriented NWs for higher pressure growth. Ge-like NWs always follow ⟨111⟩ and grow with Au-free sidewalls. © *2010 American Institute of Physics*. [doi:10.1063/1.3497079]

$Si_{1-x}Ge_x$ alloy nanowires (NW) grown using the vapor-liquid-solid (VLS) technique have attracted attention for their potential applications in NW electronics.[1] The electronic properties of SiGe NWs can be tuned by varying the Ge composition, X.[2–4] Therefore, previous research has focused on tuning X by varying chemical vapor deposition (CVD) parameters[5,6] and NW diameter[7] as well as the measurement of the resulting NW energy band gaps[2–4] for SiGe NWs grown under high vacuum conditions. The CVD parameters investigated include the total precursor pressure, the Ge:Si precursor flow ratio, which determines precursor partial pressures, and the substrate temperature. Givan *et al.*, showed that SiGe NW composition could be tuned by changing total precursor pressure while keeping flow ratio and substrate temperature constant.[5] Zhang *et al.*, showed that X falls as diameter (D) reduces for NWs with $D < \sim 60$ nm.[6] Lastly, Lew *et al.*, showed that SiGe NWs become Si rich with increasing temperature.[7]

Here, we confirm similar trends for SiGe NWs grown using ultra high vacuum (UHV) CVD via Au catalyzed VLS using mixtures of disilane (Si_2H_6) and germane (GeH_4). We also find that the alloy NWs can adopt either Si-like or Ge-like characteristics. With increasing X, $Si_{1-x}Ge_x$ NWs transition from a Si-like to a Ge-like morphology at a critical Ge composition, which depends on growth temperature, $X_{min}(T)$ and on D for NWs grown at $T=500$ °C. Si-like NWs follow trends similar to those previously described for Si NWs. SiGe NWs with $X < X_{min}(T)$ that are grown at the lowest total precursor pressures grow along ⟨111⟩ with Au decorated sidewalls. Those grown at higher total precursor pressures follow ⟨112⟩ and grow with Au free sidewalls.[8,9] In contrast, Ge-like SiGe NWs grown with $X > X_{min}(T)$ follow ⟨111⟩ and grow with Au-free sidewalls regardless of precursor pressure, similar to Ge NWs.[8] We find that Ge contents as low as 0.13 can stabilize Au-free growth of epitaxial [111]-oriented (i.e., "vertical") NWs. Since Au acts as a deep trap level in SiGe which limits the minority carrier lifetime, this result could have implications for nanoelectronic applications of epitaxial SiGe alloy NWs.

SiGe NWs were grown in a UHV CVD (base pressure $=5\times10^{-10}$ torr) system with an *in situ* metal deposition capability, the details of which are described elsewhere.[10] Multisized Au seed diameter distributions were formed by varying the substrate temperature during Au deposition onto Si(111) by thermal evaporation. These multisized seed ensembles enable efficient investigation of any NW diameter-related effects within a single growth run. We deposited 2.5 ML of Au [1 monolayer, or ML is 7.84×10^{14} cm^{-2} on Si(111)] at $T=500$ °C followed by an additional 1.5 ML of Au at $T=450$ °C. Using a deposition rate of 3/4 ML/min results in formation of $\sim10^7$ cm^{-2} Au islands with $D=200$ nm and $\sim10^9$ cm^{-2} Au islands with $D=60$ nm. SiGe NWs were grown using undiluted Si_2H_6 and GeH_4 at $T=400$ and 500 °C. Various total precursor pressures in the 3–160 mtorr range were employed using $GeH_4:Si_2H_6$ flow ratios in the 1:2 to 8:1 range. The total precursor pressure was regulated to a constant value for each growth run and each precursor partial pressure was determined by the flow ratio. NW morphology was assessed using scanning electron microscopy (SEM). Z-contrast scanning transmission electron microscopy (STEM) was employed to detect the presence or absence of Au on the NW sidewalls.[8,9] X was determined using energy dispersive x-ray spectroscopy (EDX) within the TEM. Details of the EDX analysis are presented in Ref. 9.

We find that X can be tuned by varying any of the three growth parameters: total precursor pressure, substrate temperature or $GeH_4:Si_2H_6$ flow ratio. Figure 1 summarizes the effect of total precursor pressure and substrate temperature on X for both 60 and 200 nm diameter NWs as measured using EDX. EDX measurements were acquired near the NW tip to avoid collecting x-rays from the Ge-rich shell that may form due to uncatalyzed sidewall deposition during growth.[11] The taper evident on the NWs shown in Fig. 2(e), below results from this sidewall deposition. As can be seen in Fig. 1(a), X increases as the total precursor pressure rises when $GeH_4:Si_2H_6$ flow ratio and temperature are held constant at both $T=400$ and 500 °C. Figure 1(b) reveals that X decreases with increasing T when $GeH_4:Si_2H_6$ flow ratio and total precursor pressure are held constant. As expected, X increases with increasing $GeH_4:Si_2H_6$ flow ratio (increasing GeH_4 partial pressure) at constant T and total pressure. Similar to the results of Zhang, *et al.*,[6] we do not find a significant

[a)]Electronic mail: jeff.drucker@asu.edu.

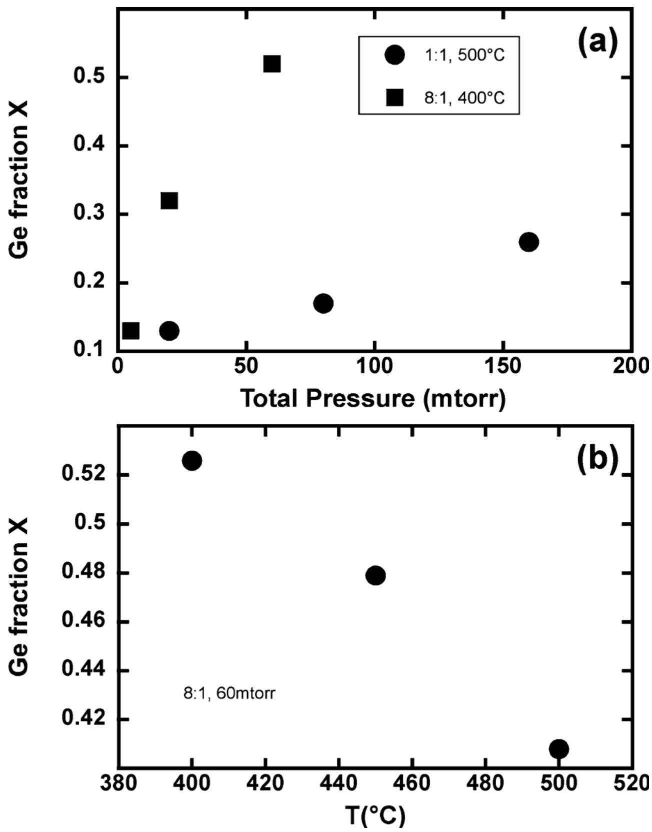

FIG. 1. Effect of CVD parameters on X for both 60 and 200 nm diameter NWs measured using EDX. (a) X vs total pressure at the indicated $GeH_4:Si_2H_6$ flow ratio and T. (b) plots X vs growth T at the indicated $GeH_4:Si_2H_6$ flow ratio and total pressure.

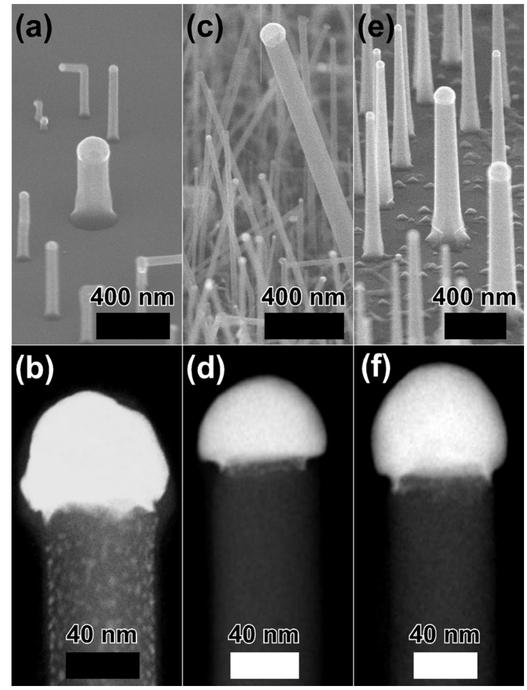

FIG. 2. Summary of NWs that adopt Si-like or Ge-like characteristics for SiGe NWs grown at T=500 °C. (a), (c) and (e) are SEM images taken 60° away from normal toward $[11\bar{2}]$. [(b), (d), and (f)] are Z-contrast STEM images of NWs from the same growth runs as (a), (c), and (e), respectively. (a) and (b) were grown using total pressure=10 mtorr and $GeH_4:Si_2H_6=1:2$, yielding NWs with X=0.11. (c) and (d) were grown using total pressure=80 mtorr and $GeH_4:Si_2H_6=1:4$, yielding NWs with X=0.05. (e) and (f) were grown using total pressure=160 mtorr and $GeH_4:Si_2H_6=4:1$ yielding NWs with X=0.36. (a)–(d) are representative of NWs that adopt Si-like characteristics. (e) and (f) are representative of NWs that adopt Ge-like characteristics.

variation in X as a function of NW diameter in the 60–200 nm diameter range that we investigated.

Besides the ability to tune X, we have also determined that the SiGe NWs can adopt Si-like or Ge-like characteristics as illustrated in Fig. 2. A Si-like NW is distinguished from a Ge-like NW by its preferred growth orientation and the presence or absence of Au on its sidewalls. Si-like NWs grown at low total precursor pressures grow along ⟨111⟩ with Au decorated sidewalls and those grown at higher total precursor pressures will grow along ⟨112⟩ with Au-free sidewalls. We have previously detailed this behavior for growth of Si NWs with D>20 nm. By analogy, we believe that growth of Si-like NWs at a low total precursor pressure allows liquid AuSiGe to spread from the seed,[9] lowering the high surface energy of the {112} sidewall facets to stabilize "vertical" growth along [111]. Growth at higher precursor pressures alters the energy balance and prevents liquid AuSiGe from spreading along the Si-like NW sidewalls. As a consequence, the NW finds it energetically favorable to kink toward ⟨112⟩[8] since NWs following that direction are bound by lower energy facets that lie on the Si equilibrium crystal shape. SiGe NWs exhibiting Si-like characteristics are shown in Figs. 2(a)–2(d). On the other hand, Ge-like SiGe NWs mimic the behavior of Ge NWs. Ge NWs with D>20 nm always grow along [111] with Au-free sidewalls,[8] as shown in Figs. 2(e) and 2(f).

The major factor determining whether SiGe NWs adopt Si-like or Ge-like characteristics is X, as shown in the "phase diagrams" of Fig. 3. Specifically, SiGe NWs will adopt Ge-like characteristics above a temperature dependent minimum Ge content, $X_{min}(T)$. SiGe NWs with $X<X_{min}(T)$ adopt Si-like characteristics. As shown in Fig. 1(a), X increases with increasing total pressure as well as increasing $GeH_4:Si_2H_6$ flow ratio. Therefore, X increases diagonally going from the bottom-left to the upper-right of the plots of Fig. 3 as indicated by the X values next to the plot symbols. As shown in Fig. 3(b), $X_{min}(400\ °C)$ lies somewhere between 0.17 and 0.22 for both the 60 nm and 200 nm diameter NWs. In contrast, $X_{min}(500\ °C)$ depends on NW diameter as shown in Fig. 3(a). For the 60 nm diameter NWs $X_{min}(500\ °C)$ lies somewhere between 0.11 and 0.13 whereas the 200 nm diameter NWs have $X_{min}(500\ °C)$ somewhere between 0.11 and 0.17; NWs with D=200 nm adopt Si-like characteristics at X=0.13.

The results shown in Fig. 3 suggest that a combination of factors participate in the adoption of Si- or Ge-like characteristics. As X increases, the energy of the {112} NW sidewalls bounding ⟨111⟩-oriented NWs decreases since Ge(112) is a lower energy surface than Si(112).[12] Once $X \geq X_{min}(T)$ the energy of the {112} NW sidewalls becomes low enough to prevent liquid AuSiGe from spreading along the NW sidewalls for all precursor pressures and the energy of the ⟨111⟩ orientation falls below that of ⟨112⟩. Essentially, as X increases, liquid AuSiGe is less likely to spread and the need for Au on the NW sidewalls to stabilize ⟨111⟩-oriented growth is reduced. Consequently, the NWs follow [111] and grow normal to the substrate as shown in Fig. 2(e). The diameter dependence in $X_{min}(500\ °C)$ fits within this de-

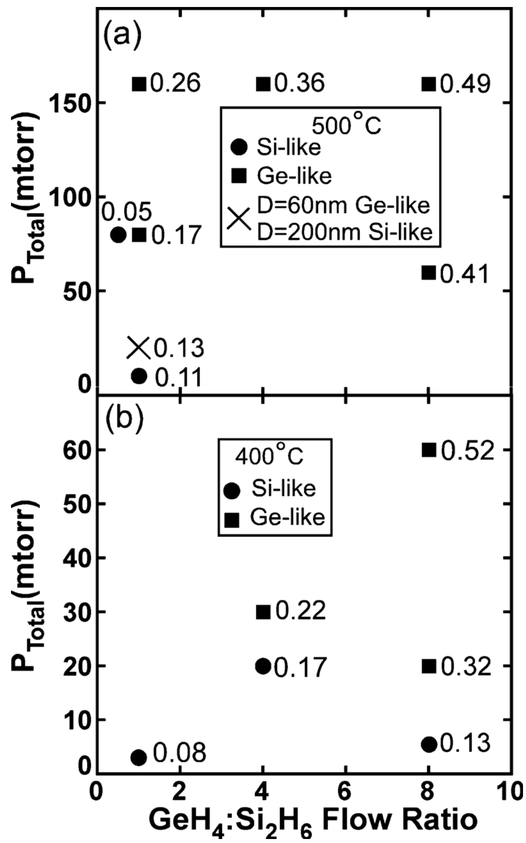

FIG. 3. Morphology "phase diagrams" detailing growth conditions producing SiGe NWs that adopt Si-like or Ge-like characteristics at (a) T=500 and (b) 400 °C. The Ge content, X, is shown at each point. Each point corresponds to both 60 nm and 200 nm diameter NWs except for the "X" in the 500 °C plot, which corresponds to Ge-like growth for the 60 nm NWs and Si-like growth for the 200 nm diameter NWs.

scription since we have recently found that liquid AuSi is less likely to spread along the sidewalls of smaller diameter NWs than larger diameter NWs.[9,13] Thus, the lower X_{min} for NWs with D=60 nm than for NWs with D=200 nm shown in Fig. 3(a) supports this scenario. Finally, we note that the diameter dependence indicated by the "X" plot symbol in Fig. 3(a) suggests that Ge sidewall deposition is not a major contributing factor to the suppression of liquid seed spreading along the NW sidewalls. We base this conclusion on the supposition that Ge sidewall deposition is the same for NWs with D=60 or 200 nm but liquid spreads from the seed only for the NWs with larger D.

In conclusion, we have shown that the Ge content of epitaxial SiGe alloy NWs can be tuned by varying any of the CVD growth parameters investigated: total precursor pressure, $GeH_4:Si_2H_6$ flow ratio or substrate T. We have also demonstrated that SiGe NWs can adopt either Si-like or Ge-like characteristics. We find that epitaxial [111]-oriented, "vertical" SiGe NWs can be grown with Au-free sidewalls with $X \geq 0.13$. The ability to control alloy content and growth direction by varying CVD growth parameters provides latitude for architecture design that may be crucial for technological application.

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