Effects of Surface Chemical Structure on the Mechanical Properties of Si$_{1-x}$Ge$_x$ Nanowires


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ABSTRACT: The Young’s modulus and fracture strength of Si$_{1-x}$Ge$_x$ nanowires (NWs) as a function of Ge concentration were measured from tensile stress measurements. The Young’s modulus of the NWs decreased linearly with increasing Ge content. No evidence was found for a linear relationship between the fracture strength of the NWs and Ge content, which is closely related to the quantity of interstitial Ge atoms contained in the wire. However, by removing some of the interstitial Ge atoms through rapid thermal annealing, a linear relationship could be produced. The discrepancy in the reported strength of Si and Ge NWs between calculated and experimented results could be related to SiO$_2$/Si interfacial defects that are found in Si$_{1-x}$Ge$_x$ NWs. It was also possible to significantly decrease the number of interfacial defects in the NWs by incorporating a surface passivated Al$_2$O$_3$ layer, which resulted in a substantial increase in fracture strength.

KEYWORDS: SiGe, nanowire, mechanical, fracture, defect, passivation

One-dimensional (1D) semiconducting NWs possess very unique properties (including quantum confinement effects, surface sensitivity, and a low leakage current) that makes them attractive for use in functional nanosystems and next generation electronics. In addition, they have garnered considerable attention because key parameters such as diameter, length, growth direction, chemical composition, and doping level can be rationally and predictably controlled during the synthesis process for various devices.¹⁻⁷ Moreover, semiconductor NWs can be used in a wide range of applications including nanoelectronics, nanosensors, nanoresonators, light-emitting diodes, and thermoelectric energy scavengers.⁸⁻¹⁵ Si–Ge alloy systems are particularly attractive in terms of device applications. The Si–Ge system is known for its complete miscibility, which enables compositional modulation through the entire range. Compositional modulation can have an important influence on physical properties, such as electron and hole mobility, band gap, and lattice parameters.¹⁶⁻¹⁸ In particular, Si$_{1-x}$Ge$_x$ NWs have the potential for use as a material in ultrafast electronic devices and optoelectronic devices by utilizing a strained-SiGe system.¹⁹⁻²³ The operation and reliability of these nanodevices are uniquely dependent on the mechanical properties of nanowires, which are predicted to differ from their bulk counterparts due to their high surface-to-volume ratio. On the basis of recent reports, defect concentration and stress in nanosized structures can be affected by their limited size and high surface area to volume ratio, and fracture strengths would be expected to approach ideal values, since they would function similar to a perfect semiconductor crystal.²⁴,²⁵ Moreover, many researchers have reported on mechanical properties of Si and Ge NWs through both simulation and experimental data. (i) In experimental results, the Young’s modulus decreases, while fracture strength increases as the diameter of a semiconductor NW decreases. The Young’s modulus of Si NWs is higher than that of Ge NWs, while their fracture strength is typically lower than that of Ge NWs.²⁴⁻²⁶ (ii) Meanwhile, computational studies using both density functional theory (DFT) and classical molecular dynamics (MD) indicate that both the Young’s modulus and fracture strength of Si NWs is higher than that of Ge NWs.²⁷,²⁸ (iii) Furthermore, the fracture characteristics of these materials have been demonstrated in tensile experiments, while many simulation results showed ductile behavior.²⁴⁻³⁰ Computational calculations have shown that plastic deformation develops in NWs that are designed for a perfect semiconductor crystal under high tensile stress. Contrary to the calculations, the fracture behavior observed in tensile deformation is due to surface cracks that are induced by high stress.³¹,³² The contradiction between experimental and computational results for Si and Ge NWs has stimulated great deal of interest in the...
The mechanical properties of Si$_{1-x}$Ge$_x$ NWs, which contain Si and Ge atoms.

The goal of this study was to attempt to resolve the conflicting claims between experimental data and calculations through mechanical experiment in Si$_{1-x}$Ge$_x$ NWs by adjusting the Ge concentration from 0 atom % to 100 atom %. These conflicting issues can be resolved by strictly controlling the Ge content on NWs, because the mechanical properties of Si$_{1-x}$Ge$_x$ NWs as a function of Ge content have not been systematically examined to date. The mechanical properties of Si$_{1-x}$Ge$_x$ NWs were experimentally investigated by means of quantitative stress–strain measurements, which are also considered in connection with the results of calculations made by DFT calculations. The findings indicate that the chemical structure on the wire surface caused by interstitial Ge states and defect states at the SiO$_2$/Si$_{1-x}$Ge$_x$ interface cause changes in the mechanical properties of Si$_{1-x}$Ge$_x$ NWs. Hence, the data indicate that the discrepancies observed between mechanical properties and experimental data can be resolved by appropriately controlling surface defects through a passivation process using Al$_2$O$_3$.

Si$_{1-x}$Ge$_x$ NWs were synthesized by the vapor–liquid–solid (VLS) method using an ultrahigh vacuum chemical vapor deposition (CVD) system. A 2 nm thick Au film (as a catalyst) was deposited on a cleaned Si(111) substrate in a metal growth chamber at a growth pressure of $\sim 5 \times 10^{-7}$ Torr by thermal evaporation. The sample was transferred in situ to the main chamber and annealed at a pressure of $\sim 1 \times 10^{-8}$ Torr for 5 min, resulting in the formation of Au–Si alloy droplets from the Au film on the Si substrate. After the formation of droplets, Si$_{1-x}$Ge$_x$ NWs were synthesized by filling the main chamber with a mixture of SiH$_4$ and GeH$_4$ as precursors, and H$_2$ as the carrier gas, while maintaining a fixed total pressure of 2 Torr by a feedback system using a throttle valve and a baratron gauge. The Ge concentration was controlled by adjusting the ratio of the SiH$_4$ and GeH$_4$ gas to 20:0, 5:10, 20:20, 10:5, and 0:20 sccm, under a fixed H$_2$ flow of 200 standard cubic centimeters per minute (sccm); that is, this makes it possible to control the Ge content in the Si$_{1-x}$Ge$_x$ NWs from 0 to 100%. The process temperature was set to 400–450 °C because phase diagrams of Au–Si and Au–Ge indicate identical eutectic temperatures and similar growth kinetics. The grown NWs were cleaned with a dilute HF solution before measuring their chemical and mechanical properties. In order to change the chemical structure of the surface in the nanowire, an Al$_2$O$_3$ shell was grown on the Si$_{1-x}$Ge$_x$ NWs using an atomic layer deposition (ALD) system. Prior to the growth of the Al$_2$O$_3$ shell, the NWs were dipped into a dilute HF solution to remove traces of native oxides. Trimethylaluminum [Al(CH$_3$)$_3$] and H$_2$O were used as the Al precursor and the oxidant, respectively. The morphological characteristics and crystalline structures of the NWs were examined by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). Energy dispersive X-ray (EDX) analysis was employed to verify the chemical composition of the Si$_{1-x}$Ge$_x$ NWs. The microstructure and chemical composition of the NWs were confirmed by Raman spectroscopy. The mechanical properties of the Si$_{1-x}$Ge$_x$ NWs were measured in tensile experiments using a nanomanipulator (MM3A, Kleindeck) installed in a focused ion beam (FIB) system (Quanta 3D, FEI), and the results compared to the values obtained by DFT calculations using VASP code with the GGA-PBEsol function. The chemical structure was examined by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al Kα (1486.6 eV) source. The defect states on the NW surface were analyzed by photoluminescence (PL) with the excitation source of a He–Cd laser (325 nm) in a cooling system using a closed-cycle liquid helium cryogenerator (7 K).

All of the Si$_{1-x}$Ge$_x$ NWs that were grown vertically at various inlet gas ratios had similar diameters and lengths. As a result, the experimental conditions were such that tensile stress data for NWs was relatively reliable. Figure 1a,b shows SEM and TEM images of the Si$_{1-x}$Ge$_x$ NWs grown at a gas flow rate of 5:10 sccm (SiH$_4$/GeH$_4$)$_x$ of 100 atom % and 50 atom %, respectively. The morphology characteristics and crystalline structures of the NWs were investigated by HRTEM. All of the NWs were grown in a single crystalline form with a growth direction of [111] and smooth sidewalls were observed, regardless of the alloy composition (Supporting Information Figure S1). The selected area electron diffraction (SAED) pattern in the inset of Figure 1b shows the image contrast with the growth direction of the NWs is [111] and the crystalline structure is a face centered cubic (fcc) phase, which is in good agreement with NCEMSS simulations. The chemical composition of the NWs was confirmed by Raman spectroscopy. The results show that the NWs were synthesized by the vapor–liquid–solid (VLS) method using an ultrahigh vacuum chemical vapor deposition (CVD) system.
NWs as a function of inlet gas ratio was confirmed by EDX analysis as shown in Figure 1c. The results are summarized in Table 1.

Table 1. Experimental Conditions for Inlet Gas Ratio of SiH₄ to GeH₄ and the Atomic Concentrations, As Measured by EDX in Various Si₁₋ₓGeₓ NWs

<table>
<thead>
<tr>
<th>inlet gas ratio (sccm)</th>
<th>GeH₄</th>
<th>Ge content (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄</td>
<td>GeH₄</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>61.3</td>
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<td>20</td>
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<td>5</td>
<td>10</td>
<td>94.1</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>100</td>
</tr>
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</table>

To investigate the mechanical properties of Si₁₋ₓGeₓ NWs as a function of Ge content, tensile stresses were carried out by stretching the wire using a nanomanipulator in a FIB system. For the tensile test, one end of a NW was placed in contact with a tungsten tip using e-beam assisted Pt deposition, and the NW grown on the Si substrate was picked up using a nanomanipulator. The other end of the NW was vertically welded onto a cantilever by Pt deposition (Supporting Information Figures S2 and S3). A NW prepared in the nanomanipulator system, as shown in Figure 2a, was subsequently pulled in a direction parallel to the NW with a tension rate of 1.9 × 10⁻⁹ m/sec until an abrupt fracture occurred, as shown in Figure 2b. Flow stress is calculated by dividing the load force (N) by the area (m²). The load force was obtained by means of a force measurement system attached to a cantilever, and the cross-sectional area of the NW was measured from TEM samples prepared by the FIB method (Supporting Information Figure S4). Si₁₋ₓGeₓ NWs as a function of Ge content (x = 0, 0.61, 0.74, 0.94, and 1) with diameters of 70–80 nm were used in the tensile experiments.

The strain on the NWs can be directly measured from the series of SEM images taken during the tensile experiments. Figure 2c,d shows the initial state of a loaded NW and the specific state just before a fracture. The strain is calculated by the formula \( \varepsilon = (L_f - L_i)/L_i \). No evidence for NW slippage was observed at either end, indicating that the Pt deposition was sufficiently strong to fix the NWs. The stress–strain curves resulting from the tensile experiment are plotted in supporting Supporting Information Figure S5. Figure 2e shows the measured Young’s modulus, fracture strength, and strain of Si₁₋ₓGeₓ NWs as a function of Ge content. The Young’s modulus of the NWs decreases gradually with increasing Ge content, which indicates an approximately linear relation between the relative composition of Si and Ge. On the basis of the reported Young’s modulus for Si and Ge NWs with a [111] direction, the measured values reported using our system are comparable to values that have been previously reported through experiments and calculations; Wu et al. reported on calculations of elastic modulus for materials, such as Si NWs, of 139–165 GPa and Ge NWs of 106–125 GPa. All of the reported data in cases of both experiment and calculation showed that the elastic modulus of Ge NWs is lower than that of Si NWs, as summarized in Table 2.

Table 2. Reported Mechanical Properties for Si and Ge Nanowires

<table>
<thead>
<tr>
<th></th>
<th>experimental value (111)</th>
<th>calculated value (111)</th>
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</thead>
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<tr>
<td></td>
<td>elastic modulus (GPa)</td>
<td>tensile strength (GPa)</td>
</tr>
<tr>
<td></td>
<td>Si NW</td>
<td>158</td>
</tr>
<tr>
<td></td>
<td>Ge NW</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>elastic modulus (GPa)</td>
<td>tensile strength (GPa)</td>
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<tr>
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<td>139–165</td>
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<tr>
<td></td>
<td>Ge NW</td>
<td>106–125</td>
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An overall difference in Young’s modulus between our measured value in Figure 2e and the calculated values in Table...
2 was found (i.e., the measured values of both Si and Ge NWs are slightly smaller than the calculated values). Stan et al. suggested that the difference between the molecular volumes of the inevitably formed native oxide shell (<1 nm) and the atomic volume of Si(Ge) core can cause radial compressive stress, which would induce biaxial strain in NWs, thus decreasing the Young’s modulus in Si(Ge) NWs. Similarly, the lower values for the Young’s modulus measured in our system (compared to the calculated value) can be explained by the effect of the formation of a native oxide shell. However, the fracture strength and strain of Si$_{1-x}$Ge$_x$ NWs as a function of Ge content do not show a linear relationship, which differs greatly from the behavior associated with the change in moduli. The fracture strength and strain of the NWs decreases somewhat in the specific region of Ge content ($x = 0.61 - 0.94$). Interestingly, this phenomenon is unexpected, because the fracture strength and strain of NWs could be expected to increase gradually in proportion to Ge content.

To investigate this unexpected result for the mechanical properties in Si$_{1-x}$Ge$_x$ NWs, we examined the relative concentration of Ge and Si atoms, and chemical states in the NWs using Raman spectroscopy, EDX, and XPS. By comparing the content of atomic Ge concentration between EDX and Raman, it was possible to verify the presence or absence of interstitial Ge atoms in this study. Raman shifts were measured as a function of the inlet gas ratio, as shown in Figure 3a. The Raman spectrum is characterized by three dominant peaks, which correspond to specific scattering frequencies from optical phonons involving Ge—Ge ($\omega \approx 295$ cm$^{-1}$), Si—Ge ($\omega \approx 415$ cm$^{-1}$), and Si—Si ($\omega \approx 505$ cm$^{-1}$). When the Si—Ge alloy system is fully relaxed, the frequencies that are dependent on Ge composition $x$ are given as follows:

$$\omega (\text{cm}^{-1}) = 280.8 + 19.37x \quad (\text{Ge—Ge}) \quad (1-1)$$

$$\omega (\text{cm}^{-1}) = 400.0 + 22.07x - 36.14x^2 + 83.73x^3 \quad - 88.54x^4 \quad (\text{Si—Ge}) \quad (1-2)$$

$$\omega (\text{cm}^{-1}) = 521.2 - 67.91x \quad (\text{Si—Si}) \quad (1-3)$$

Using these formulas we calculated the Ge content ($x$) in the NWs from the Raman peaks. The Ge concentration (atom %) extracted from both EDX (Figure 1c and Table 1) and Raman (Figure 3a) data appears to be a function of inlet gas ratio in the graph of Figure 3c. According to the above formula, the Ge—Ge bonding peak should be shifted toward a higher frequency with increasing Ge concentration. That is to say, Raman peaks reflect Si and Ge atoms that are incorporated substitutionally in the NWs. EDX analysis, meanwhile, can detect Si and Ge atoms irrespective of the substitutional or interstitial incorporation in the NWs. We observed that the Ge concentration obtained from the Raman data is lower than that obtained from EDX data, which means that excess Ge atoms are present that do not contribute to the cubic unit cell structure of the Si—Ge alloy system. Thus, the noticeable discrepancy in the Ge concentration between the EDX and Raman measurements can be attributed to the presence of the interstitial incorporation of Ge atoms during the synthesis process when a high GeH$_4$ gas flow rate is used. XPS was performed to collect information related to the chemical state of excess Ge atoms in the NWs. Figure 3b shows the Ge 3d core level spectra of the Si$_{1-x}$Ge$_x$ NWs as a function of the fraction of Ge. The main component in the Ge 3d core level located at ~29.5 eV is related to pure Ge bonding (Ge—Ge, Ge$^0$). To obtain detailed information on the chemical states of Si—Ge and interstitial Ge atoms in the NWs, the Ge 3d spectra were deconvoluted and fitted using a 3d$_{3/2}$ and 3d$_{5/2}$ with a spin—orbit splitting of 0.585 eV and an intensity ratio of 0.67. We used electronegativity values of 1.90 for Si and 2.01 for Ge. Charge transfer induces a decrease in the binding energy of the Ge$^0$ core level by forming Si—Ge bonds in a Si—Ge alloy system. Since the differences in chemical shift or binding energy between Si—Ge and Ge—Ge are very small (within 0.15 eV), it becomes difficult to distinguish their states due to limitations of spectroscopy resolution. Therefore, Ge 3d can be divided with only two states corresponding to the sum of Ge—Ge (Ge$^0$) and Si—Ge (SG) bonding, and interstitial Ge atoms (Ge$_i$) as elemental atoms. We observed that the width of the main peak at ~29 eV increases slightly in proportion to Ge content in the NWs, and a clear shoulder can be seen in the peak of Si$_{1-x}$Ge$_x$ NW ($x = 0.9$), indicating the generation of another Ge$_i$ state, as shown in Figure 3b. The Ge$_i$ state is shifted to a lower binding energy by ~0.25 eV from the peak assigned to the Ge$^0$ + SG states, which is consistent with the previously observed findings regarding binding energy. On the basis of XPS results, we propose that the excessive Ge atoms shown at the top of Figure...
3c can be attributed to the interstitially incorporated Ge atoms (Ge$_i$ state) in the NWs. The oxide peak at a higher binding energy of $\sim$33 eV was also deconvoluted with Ge$^{1+}$ at 30.35 eV, Ge$^{2+}$ at 31.20 eV, Ge$^{3+}$ at 32.05 eV, and Ge$^{4+}$ at 32.9 eV. Consequently, since the generation of interstitial Ge atoms can induce internal strain, this can significantly affect the mechanical properties of the NWs. Thus, the presence of excess Ge$_i$ atoms can explain the differences reported between experimental findings and calculations. To remove Ge$_i$ atoms, we employed a rapid thermal annealing (RTA) process at a temperature of $\sim$400 °C below the process temperature, which is considered to be an effective method for removing interstitial atoms incorporated into a wire throughout out-diffusion by heat energy. After the RTA, the crystalline structure and surface morphology of the NWs were examined by TEM. Neither surface damage nor changes in the crystalline structure could be observed. Furthermore, we rechecked the presence of Ge$_i$ atoms by using Raman and XPS tools (Supporting Information Figure S6). The Ge concentration extracted from the Raman spectra and EDX as a function of inlet gas ratio (Supporting Information Figure S6) was recalculated using eq 1-1; the quantity was identical compared to a value obtained in an EDX, as expressed in the bottom graph of Figure 3c. It should be noted that we actually achieved a Ge$_i$ state that was remarkably decreased in the NWs by measuring the XPS as shown in Supporting Information Figure S6b. In particular, the shape of the Ge–Ge peak in the Raman spectra verified the effect on Ge$_i$ atoms in the NWs. For a more detailed description of the contribution of the Ge$_i$ state, we analyzed the Raman spectra of the Ge–Ge peak before and after RTA in the case of the Si$_{10}$Ge$_{90}$ NWs containing the largest amount of Ge$_i$ atoms (Supporting Information Figure S6c). This figure shows the fitted Raman spectra of the Ge–Ge peak in Si$_{10}$Ge$_{90}$ NWs before and after RTA. At the top of Supporting Information Figure S6c, the shape of the Ge–Ge peak in the NWs was asymmetric prior to RTA. However, after the RTA of the NWs, the peak shape becomes symmetrical, as shown in the middle of (Supporting Information Figure S6c). Although some deviations in Raman line-shape symmetry, frequency, and line width are caused by the quantum confinement effect, elastic strain effect, heating effect, and electron–phonon interactions, it can be reasonably assumed that the Raman peak related to the near surface region is only determined by the effect of a three-dimensional (3D) confinement effect. We deconvoluted the Raman spectra of the Ge–Ge peak in the Si$_{10}$Ge$_{90}$ NW into three contributions with atomic vibrations from the crystallite core at $\sim$299 cm$^{-1}$, near surface region at $\sim$297 cm$^{-1}$, and disordered atoms at $\sim$290 cm$^{-1}$, respectively. Therefore, the Raman peak related to the presence of disordered Ge atoms could be assumed to be Ge$_i$ atoms that are a part of the cubic unit cell structure of the NWs. In particular, the peak intensity at $\sim$290 cm$^{-1}$ associated with the Raman scattering from disordered Ge atoms is decreased substantially after RTA, which is consistent with the XPS results shown in Supporting Information Figure S6b, that is, a significant decrease in Ge$_i$ atoms was found as the result of the RTA. Moreover, in the Ge NW the Ge$_i$ level is very low, which is consistent with the fracture strength and strain characteristics associated with Ge NWs. Finally, we conclude that the peak from the presence of disordered atoms is due to a combination of 3D confinement and the effects of tensile strain.

We attempted to collect information related to the mechanical properties of Si$_{1-x}$Ge$_x$ NWs without an effect on Ge$_i$ atoms in the wire after the RTA process. Figure 4 shows the measured Young’s modulus, fracture strength, and strain for the NWs ($x = 0, 0.61, 0.72, 0.90$ and $1.00$, after RTA). Astonishingly, after the RTA process the fracture strength and fracture strain of the NWs show a linearly increasing relationship that is proportional to the Ge content, as indicated by a red triangle, which is consistent with the expectation that the values would increase in a linear manner from $x = 0$ to $x = 1$. The Young’s modulus data shows almost the same results before the RTA process, because the linear slope of the stress–strain curve at any point can represent Young’s modulus in a solid. That is to say, in the case where the change in tendency of stress and strain is the same, unfortunately, Young’s modulus cannot be used as an indicator of strain–stress as shown in Figure 4. Considering these changes in the fracture strength and strain of Figure 4, we concluded that the Ge$_i$ atoms intimately affect the mechanical properties of NWs.

To systematically investigate the change in the mechanical properties as a function of Ge content and the role of Ge$_i$ atoms in the Si$_{1-x}$Ge$_x$ NWs, we carried out DFT calculations. Figure 5a shows the stress–strain curves for the Si$_{1-x}$Ge$_x$ system obtained from a DFT calculation. The results of tensile stress simulation in the supercell structure of Si$_{1-x}$Ge$_x$ show improved mechanical properties with a decreased Ge content compared to our experimental results in Figure 4. The slope of the stress–strain curves, which represents the Young’s modulus, is inversely proportional to the Ge content. This is in agreement with reported data indicating that the Young’s modulus of Si NWs is higher than that of Ge NWs. Interestingly, there are practical differences between simulations and experimental data. For example, the fracture strength increases linearly with the amount of Si content in Si$_{1-x}$Ge$_x$ NWs in the calculation, so the strength of Si NWs is higher than that of Ge NWs. However, the experimental results indicate that it decreases linearly with the amount of Si content in the wire, as shown in Figure 4. Moreover, the strain and stress graph shows ductile

**Figure 4.** Young’s modulus, fracture strength, and strain of the Si$_{1-x}$Ge$_x$ NWs ($x = 0, 0.61, 0.72, 0.90$ and $1.00$, after RTA).
behavior and not fracture formation, which is contrary to our experimental results. First, to determine the role of Gei atoms in the mechanical properties of Si$_{1-x}$Ge$_x$ NWs, we calculated the stress–strain curve of the Si$_{0.25}$Ge$_{0.75}$ supercell structure with and without Gei atoms, as shown in Figure 5b. In the case of the Si$_{0.25}$Ge$_{0.75}$ structure with Gei atoms, the calculated fracture stress and strain decreased slightly, which is consistent with our results for the tensile stress of the NWs before the RTA process. Moreover, the ductile behavior of the supercell structure changes to fracture behavior under the tensile stress of the structure with Gei atoms present (Supporting Information Figure S7). Many researchers have reported that NWs exist in the form of a perfect crystal, so fracture strengths would be expected to have the ideal values of the crystal. However, the experimental data shows that the strain–stress curve of Si$_{1-x}$Ge$_x$ NWs behaves analogous to a fracture type change with lower stress compared to the ideal values that are found for a perfect crystal structure. The characteristic change clarifies the effect of defect states such as Gei atoms that are present in the wire. Thus, the decrease in fracture strength and strain of the NWs can be attributed to as increase the level of Gei atoms in a specific region of Ge ($x = 0.61−0.90$).

Although the calculation data containing Gei atoms indicate a fracture type change during the structural deformation process, the data are still higher than our experimental values. The calculated results could explain the changes in modulus in the tensile experiments, while the results could not be used to elucidate the results of the fracture strength and strain. On the basis of reported calculation data, fracture behavior can be generated by defects on the wire surface, resulting in the development of cracks in the wire surface.

In practice, since native oxides are inevitably formed in NWs on the wire surface during the growth process and post process, various defect states can be formed at the interface, thus inducing fracture behavior and decreased fracture strength in NWs in the experimental results. These interface defects such as oxygen vacancies, silicon dangling bonds, and oxygen dangling bonds (nonbridging oxygen hole centers) are formed by strained Si–O bonds at the interface between oxide and silicon (germanium). Therefore, we hypothesized that the fracture strength and strain are closely associated with a surface defect state on the wire. To determine the effect on the surface defects that influence the mechanical properties of the wire, the surface defect state must be rigorously controlled. Since fracture strength is particularly sensitive at the side surface of the NWs, the opposite tendencies for fracture strengths of Si NW and Ge NW between calculations and experiments can also be closely related to the presence or absence of surface defects. The findings showing that the fracture strength of Si NWs is decreased compared to Ge NWs indicates that the difference in the defects between Si NW and Ge NW surfaces can cause the discrepancy between the calculated and experimental values for NWs. Since Al$_2$O$_3$ films are generally known as a passivation material that suppresses oxidation, we deposited an Al$_2$O$_3$ film on the Si$_{1-x}$Ge$_x$ NW to prevent an interfacial reaction between the Si$_{1-x}$Ge$_x$ surface and the oxide shell. Originally, native oxides such as SiO$_2$ and GeO$_2$ can be easily formed in air, which generates defects at the interface between the oxide and the NW surface.

![Figure 5.](image1.png)

Figure 5. (a) Stress–strain curves of Si$_{1-x}$Ge$_x$ supercell structures ($x = 0, 0.25, 0.5, 0.75,$ and 1) from DFT calculation. (b) Stress–strain curve of Si$_{0.25}$Ge$_{0.75}$ supercell structure including Gei.

![Figure 6.](image2.png)

Figure 6. (a) Stress–strain curves and (c) low-temperature PL spectra of Si$_{1-x}$Ge$_x$ NWs ($x = 0, 0.61,$ and 1) before and after Al$_2$O$_3$ deposition on NWs. (b) Young’s modulus, fracture strength, and fracture strain of the Si$_{1-x}$Ge$_x$ NWs with Al$_2$O$_3$ shell.
to remove native oxides from the wire, the Si$_x$Si$_{1-x}$Ge$_x$ and Ge NWs were cleaned with a dilute HF solution, and a 2 nm Al$_2$O$_3$ shell was then grown on the NWs using an ALD system (Supporting Information Figure S8). In order to verify the effect of surface defects on the wire (not the interstitial Ge atom), we examined the mechanical properties of the Si$_x$Si$_{1-x}$Ge$_x$ NWs ($x = 0, 0.61,$ and 1), which contain almost no Ge$_x$ states in the wire, as confirmed by XPS and Raman spectra, as shown in Figures 3 and Supporting Information Figure S6. Thus, this eliminates the effect of Ge$_x$ atoms in Si$_x$Si$_{1-x}$Ge$_x$ and Ge NWs. Figure 6a clearly shows the opposite tendency in the stress–strain curves for Si$_x$Si$_{1-x}$Ge$_x$ NWs ($x = 0, 0.61,$ and 1) depending on Al$_2$O$_3$ shell deposition. Fracture stresses in the NWs surrounded by the Al$_2$O$_3$ shell are significantly increased with decreasing Ge content compared to the NWs without shell. However, a relatively slight increase of fracture stress was found in the Ge NWs compared to that of the Si$_x$Si$_{1-x}$Ge$_x$ NWs ($x = 0, 0.61,$ and 1). Since the strength of alumina is a few hundred megapascals, the NW fracture strength would not be expected to be affected by the Al$_2$O$_3$ shell. $^{47}$ Figure 6b shows the Young’s modulus, fracture strength, and fracture strain for the NWs with an Al$_2$O$_3$ shell as a function of Ge content. The change with Ge content for Young’s modulus and fracture strain of the NWs surrounded by Al$_2$O$_3$ was not significantly different from that of the results observed from the tensile experiment of NWs after RTA, as shown in Figure 4. Surprisingly, however, the change in the fracture strength of the NWs surrounded by Al$_2$O$_3$ is consistent with the results calculated in the tensile test of a supercell structure. Because of the increase in fracture strength, the modulus increases with decreasing Ge content compared to Figure 4. By decreasing the surface defect state, the fracture strength of pure Si$_x$Si$_{1-x}$Ge$_x$ NWs is in general agreement with the results of our calculations, which indicate a linear decrease with increasing Ge content, as shown in Figure 6b. Photoluminescence was measured to analyze the surface defect state in the wire as a function of Al$_2$O$_3$ shell deposition. Figure 6c shows PL spectra of Si$_x$Si$_{1-x}$Ge$_x$ NWs ($x = 0, 0.61,$ and 1). The PL intensity is extremely sensitive at the measuring temperature, which can decrease PL intensity with an increase in measuring temperature. The thermal quenching of the luminescence is considered to originate from the thermal ionization of electrons or holes trapped on the defect centers in the wire, as confirmed by DFT calculations, the structural evolution in the wire can be changed from ductile to fracture when a defect state such as interstitial Ge atoms is present in the wire. After decreasing the interstitial Ge atoms throughout the RTA process, the fracture strength and strain of NWs can be expressed as a linear relationship as a function of Ge content. In particular, the findings indicate that the difference in fracture strength between the calculated value and experimental results can be attributed to the presence of surface defects at the interface between the SiO$_2$ and the NWs surface. Finally, it is possible to control defect formation by using a surface passivated Al$_2$O$_3$ layer that blocks the diffusion of oxygen.

**ASSOCIATED CONTENT**

**Supporting Information**

Figures and movie of tensile experiment of SiGe NW. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was partially supported by the IT R&D program of MKE (KI002083, Next-Generation Substrate Technology for High Performance Semiconductor Devices) and the Korea Research Institute of Standards and Science under the Metrology Research Center project.

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