Anomalous Surface Doping Effect in Semiconductor Nanowires

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ABSTRACT: Surface doping is being used as an effective approach to improve the mechanical, optical, electronic, and magnetic properties of various materials. For example, experimental studies have proven that rare-earth element doping can enhance the optical properties of silicon nanostructures. However, the majority of previous investigations focused on either bulk materials or nanosized spherical crystals. Here we present a comparative study on semiconducting germanium (Ge) nanowires with and without surface doping by using multiple integrated characterization probes, including high resolution scanning/transmission electron microscopy (SEM/TEM), in situ high pressure synchrotron X-ray diffraction (XRD), and Raman spectroscopy. Our results reveal that under pressure the stability of the Ge-I phase (diamond structure) in erbium (Er)-doped Ge nanowires is enhanced compared to undoped Ge nanowires. We also found an increased stability of the Ge-II phase (body centered tetragonal structure) in Er-doped Ge nanowires during decompression. Furthermore, the presence of Er doping elevates the transition kinetics by showing a smaller pressure span needed for a complete Ge-I to Ge-II phase transformation. In contrast, Er doping has a negligible impact on the mechanical properties of Ge nanowires under high pressure, exhibiting a very different mechanical behavior from other foreign element-doped nanostructures. This anomalous doping effect was explained based on surface modification and decoration. These findings are of both fundamental and applied significance, because they not only provide a thorough understanding of the distinct role of surface doping in nanoscale materials, but also yield insight with regard to a given material’s design for favorable properties in semiconductor nanostructures.

INTRODUCTION

The semiconductors germanium (Ge) and silicon (Si) have been widely used in transistors, optics, solar cells, and optoelectronic devices. It is not an exaggeration to say that these semiconductors laid the foundation of the modern electronic device industry. For instance, these semiconductors are a crucial constituent material in microprocessor chips, the central component of virtually every intelligent system from a simple calculator to a missile-defense system. With the versatile properties and robust capabilities of semiconductors, one has witnessed, in the rapid development of the optoelectronics industry (for instance) within the last two decades, the radical size reduction of mobile phones from the original analog ones comparable to a large briefcase to the current digital ones as small as a thumb. While these size reductions have been accompanied by a rapid advancement in their functionality, challenges in the improvement of the capacity and stability of (nanoscale) semiconductors remain.

Due to quantum size effects at the nanoscale, the physical properties of a given material are strongly correlated with its crystal size.¹⁻³ For instance, the crystal size reduction accompanied by a shape alteration from bulk to one-dimensional structure makes semiconducting nanowires particularly suitable for fabricating advanced nanoelectronic and optical devices.⁴⁻¹⁰ In fact, a number of investigations have confirmed that Si nanowires have unique optical/electrical properties compared with their bulk counterpart.⁶⁻¹³
Meanwhile, experimental and theoretical studies have demonstrated that surface doping or interstitial impurities have profound effects on the properties of natural and synthetic materials. For example, the interstitial impurities of O, N, and C suppress the $\alpha \rightarrow \beta$ phase transition from 9 GPa in pure titanium to at least 35 GPa in the titanium alloys A-70 and Ti-6Al-4V. This phase transformation retardance increases titanium’s technological suitability in aerospace applications. Since diminishing crystal size into the nanoscale regime and introducing impurity elements into materials can both tune/tailor their properties, a more useful method for material design is to combine these two effects simultaneously to produce a nanomaterial with surface doping or interstitial impurities. Previous in situ high pressure studies have shown that the phase transition behavior of Si nanocrystals is strongly controlled by the average spatial location of impurity centers, exhibiting a striking different phase transition pathway from that of conventional bulk Si. The surface dopants are also able to significantly change the electrical characteristics of Si nanowires. However, the doping effect on Ge nanowires, in particular under high pressure, remains uninvestigated.

It is known that a certain amount of Er doped onto the surface of Ge nanowires can improve their optical properties, since the luminescence band at 1.54 $\mu$m, induced from the $^{4}I_{13/2} \rightarrow ^{4}I_{15/2}$ transition of Er ions, lies at an absorption minimum for semiconducting element-based optical waveguides. Also, given that a clear understanding of the physical properties, including phase relation, elasticity, and vibrational properties, is an essential prerequisite for the practical application of a material, we combine here the high-pressure technique (via a diamond anvil cell) with Raman spectroscopy and high-energy synchrotron XRD to investigate Ge nanowires with and without surface Er doping. The experimental data allows us to address the surface Er doping effects on the thermodynamic, vibrational, and mechanical behavior of Ge nanowires under high pressure. We find that the surface doping with Er significantly retards the phase transformation from cubic to $\beta$-Sn structure, but has little impact on the mechanical properties of Ge nanowires.

**EXPERIMENTAL SECTION**

**Fabrication of the Samples.** Undoped and Er-doped Ge nanowires were fabricated by using vapor-transport method, which has been described in detail elsewhere, and here we only...
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Two samples, undoped and Er-doped Ge nanowires, were respectively grown along [111] lattice direction by a vapor-transport method. The Er-doped Ge nanowires consist of two heterojunction structures, a Ge core with a diameter of ~50 nm and an amorphous Er-rich shell with a thickness of ~5–10 nm, as shown in Figure 1. As we know that Ge nanostructure is rather sensitive to oxygen, so during experimental processing trace amount of Ge atoms on the surface of nanowires react with oxygen resulting in Ge oxide, which was observed in undoped as well as Er-doped Ge nanowires, respectively, at ambient pressure from the XRD patterns. With pressure increasing, the poorly crystalline Ge oxide (brittle ceramic) rapidly crashed into amorphous phase and thus its X-ray signature disappeared. This rationale is supported by other literature articles with a consensus that in both samples the oxygen is binding with some Ge sites at the outer surface. At ambient conditions, the bulk Ge has a cubic diamond structure (Ge-I) with a space group of Fd3m (No. 227). It transforms to a body centered tetragonal structure with a space group of F41/32m (No. 141), commonly referred to as β-Sn phase (Ge-II), at pressure around 10.6 GPa under quasi-hydrostatic condition at room temperature, and this phase remains stable up to 50 GPa. In Er-doped Ge nanowires, the unique one-dimensional nanoscale shape plus surface doping effect lead to a markedly different scenario of pressure-induced phase transition.

Synchrotron XRD was used to probe the structural transformation in both samples under high pressure at room temperature. The XRD patterns illustrate that the phase transition from Ge-I to Ge-II in undoped Ge nanowires starts at 9.6 GPa, manifested by the emergence of one weak diffraction peak as shown in the inset of Figure 2a. At 16.7 GPa, a trace amount of the original Ge-I phase can still be observed. Upon further compression up to the highest experimental pressure of 36.4 GPa, the sample consists of pure Ge-II. The detected onset transition pressure is 1–2 GPa lower than that in bulk Ge, a phenomenon that was also observed in Si nanowires and was explained by the lower misfit strain energy needed for the formation of new phase in Si nanowires. Since Ge and Si are neighboring semiconductors on the periodic table with the similar sequence of phase transitions, it is plausible that the same phenomenon was also observed in Ge nanowires.

RESULTS AND DISCUSSION

High Pressure Measurements. A rhenium gasketed diamond anvil cell was used to conduct the high-pressure measurements. The diamond anvil cell was equipped with a pair of diamonds with a culet size of 300 μm. The nanowires were loaded into a preindented sample chamber with a size of 130 μm in diameter and ~45 μm in depth. The mixture of methanol/ethanol with volume ratio of 4:1 served as the pressure transmission medium. Several ruby balls as well as gold powders were loaded inside the same sample chamber to calibrate the sample pressure. The in situ high pressure Raman spectra were obtained via using a green laser (532 nm) as excitation source. The angle dispersive synchrotron XRD patterns were collected under compression in a diamond anvil cell. Stars, exclamation marks, and arrows denote the signals from Ge-I during phase transition, gold, and rhenium gasket, respectively. The black, green, and pink patterns represent the fraction rings were integrated to give a brief summary. Undoped Ge nanowires were made from initial heating of a carbon:Ge mixture at 850 °C for 2 h, followed by heating at 1000 °C for 1.5 h under a helium atmosphere at a flow rate of 3000 sccm (standard cubic centimeters per minute). At the end of reaction, a thick brown fluffy film was grown on the downstream Si wafer that initially was coated with a thin layer of gold catalyst. Er-doped Ge nanowires were fabricated by additional heating of the as-prepared Ge nanowires in the presence of Er(tmhd)3, (tris(2,2,6,6-tetramethyl-3,5-heptanedionato) erbium(III)) vapor in a dilute He stream at 500 °C for 1 h. The Er-doped Ge nanowires appear darker than the undoped ones.

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Synchrotron XRD was used to probe the structural transformation in both samples under high pressure at room temperature. The XRD patterns illustrate that the phase transition from Ge-I to Ge-II in undoped Ge nanowires starts at 9.6 GPa, manifested by the emergence of one weak diffraction peak as shown in the inset of Figure 2a. At 16.7 GPa, a trace amount of the original Ge-I phase can still be observed. Upon further compression up to the highest experimental pressure of 36.4 GPa, the sample consists of pure Ge-II. The detected onset transition pressure is 1–2 GPa lower than that in bulk Ge, a phenomenon that was also observed in Si nanowires and was explained by the lower misfit strain energy needed for the formation of new phase in Si nanowires. Since Ge and Si are neighboring semiconductors on the periodic table with the similar sequence of phase transitions, it is plausible that the same
mechanism dictates the phase transition pathway in Ge nanowires. The lower activation energy of dislocation and the greater dislocation propagation velocity, as well as the expanded surface area with populated defects and dangling bonds, may be the additional factors contributing to the lower transition pressure in undoped Ge nanowires.\textsuperscript{34,35}

Figure 2b shows the phase transition in Er-doped Ge nanowires under high pressure. Compared to undoped Ge nanowires, the XRD signals from Er-doped Ge nanowires are weaker in intensity. The Er dopant layer surrounding the Ge core may absorb and reflect the electromagnetic radiation resulting in the weak X-ray signals. With increasing pressure the Ge-I phase remains stable until the pressure reaches 13.0 GPa, at which one weak diffraction peak of Ge-II were observed on the XRD pattern, as shown in the inset of Figure 2b, indicating that Ge-I starts transforming into Ge-II. This phase transformation is completed at 16.5 GPa. Compared to undoped Ge nanowires, the onset pressure of the phase transition in Er-doped counterpart is more than 3 GPa higher (13 vs 9.6 GPa). These observations suggest that the Er-doped surface is energetically unfavorable for the phase transition in Ge nanowires. In Figure 3, we summarize the pressure-induced phase transitions in several Ge structures at room temperature.

Figure 3. Phase transformations of various Ge structures under high pressure at room temperature. The phase regimes are indicated with different colors: blue for Ge-I, black for Ge-II, and red for the transition region from Ge-I to Ge-II.

As a complementary tool, Raman spectroscopy was used to detect the local Raman scattering under pressure and to verify the discrepancy in the phase transitions observed in the two samples. Figure 4 illustrates the evolution of Raman spectra of samples under compression and subsequent decompression to ambient condition. For undoped Ge nanowires, the cubic phase with a Raman band near 300 cm$^{-1}$ at ambient pressure remains stable up to 11.8 GPa, as shown in Figure 4a. The high-pressure Raman spectra of Er-doped Ge nanowires show similar characteristics, as shown in Figure 4b.

Based on the fact that during a phase transition the Raman band of the original phase becomes broad and weak, we can determine the onset transformation pressure from the Raman peak width against pressure. As shown in Figure 4c for undoped Ge nanowires, the Raman bandwidth increases linearly with pressure up to 6.7 GPa; at higher pressures, it deviates from the original linear trend. The critical pressure point of 9.4 GPa is very close to the onset phase transition pressure in undoped Ge nanowires determined by the XRD measurement. Therefore, the Raman band broadening below 9.4 GPa comes from the pressure effect; but beyond 9.4 GPa, the rapid band broadening is caused by two factors: a pressure effect and the formation of Ge-II. At further higher pressure, 13.5 GPa, as shown in Figure 4a, for example, the sample consisting of Ge-II completely becomes featureless in the Raman measurement.

Upon decompression, as shown in Figure 4a and c, starting from 6.1 GPa, the sample reverts to the original diamond structure. During the entire cycle of compression and decompression, the Raman bandwidth vs pressure exhibits a slight hysteresis.

For Er-doped Ge nanowires, the determined critical pressure point is around 14 GPa, as shown in Figure 4c, which is in good agreement with the onset phase transition pressure detected by XRD. Upon decompression, as shown in Figure 4b, the Ge-II transforms back to the cubic phase with the onset pressure of 4.3 GPa, roughly 2 GPa lower than that in undoped Ge nanowires. Compared to undoped nanowires, the Er-doped Ge nanowires show a more severe hysteresis, as shown in Figure 4c, during the compression and decompression cycle. Overall, the Er doping suppresses the phase transition, regardless if the Ge nanowire is subjected to either compression or decompression.

In addition, Raman spectra can provide insight as to the electrical properties of condensed matter under high pressure. For instance, the intensity drop and eventually full disappearance of Raman bands suggests a conductor/semiconductor-metal transition.\textsuperscript{36–40} Considering the unique semiconducting property of Ge, its electrical property is related with externally applied pressure, which does not only affect its electrical resistivity but also can tune its electrical conduction (p-/n-type). A previous study has demonstrated that an electronic phase transition from semiconductor to metal takes place at \textasciitilde{}10 GPa.\textsuperscript{41} A recent paper\textsuperscript{42} revealed that pressure can tune the electrical conduction (p-/n-type) in Ge. Those studies are interesting and related with the current study, but they focused on Ge in single crystal or micрослized powder form.

In the present study, the electrical properties of undoped and Er-doped Ge nanowires were derived from the high pressure Raman spectra. We observed the Raman bands broadening with intensity drop and eventually fully disappearing in both samples, and the semiconductor-metal transition coincides with the structural transformation from cubic diamond to a $\beta$-Sn phase. For each sample, the semiconductor-metal transition pressure determined by Raman is consistent with the structural transformation pressure detected from XRD. Therefore, it is plausible to propose that the $\beta$-Sn phase is metallic without a visible Raman signature. Furthermore, the entire cycle of compression and decompression for both samples show an evident hysteresis in terms of Raman band widths against pressures, as illustrated in Figure 4c. Interestingly, we observed that the hysteresis in Er-doped nanowires is severer than that in undoped ones. Though the exact mechanism behind this difference may be elucidated by theoretical computation with the input from the experimental results, qualitatively we think the impurity-Er dopants perhaps strengthen the internal friction and elongates the structural relaxation making the decomposition-induced transition in Er-doped nanowires slower than that in undoped nanowires.

Now let us turn to the Er doping effect on the mechanical properties of Ge nanowires. We refined the XRD patterns by using Rietveld method, as shown in Figure 5a, upon which the lattice parameters of Ge-I and Ge-II in both samples were obtained. Then we carefully assessed the effect of the Er-dopant layer on the mechanical property of Ge nanowires through evaluating the change in lattice parameters of individual phase...
under pressures. Figure 5b and c show that under pressure the variations of lattice parameters in both samples are very similar (almost completely overlapped), suggesting that the two Ge nanostructures give mechanical response to the externally applied pressure without any distinguishable difference. This conclusion is further supported by the coincidence of Raman peak versus pressure in two samples, as shown in Figure 4d.

An Er-dopant layer plus a Ge core forms a so-called core−shell structure. During the high-pressure measurements, the nanowire is submerged into the liquid transmission medium, so the external forces are uniformly applied onto the Er layer, as shown in Figure 5d. Therefore, the pressure experienced by the Ge core should be lower or even totally zero, because the Er-dopant layer can uphold portion of the applied pressure or even completely shields the Ge core from the compression if the applied pressure is lower than the mechanical strength of the Er-dopant layer. If this is true, we can use this mechanism to explain the enhanced phase stability observed in the Er-doped Ge nanowires, because the additional force has to be applied in order to make Ge core reach the onset phase transition pressure. However, from Figure 5b and c, we learned that the Er-dopant surface layer has no observable influence on the mechanical properties of Ge nanowires under high pressures, and its function is just like a pressure transmission medium to transmit the force onto the Ge core without any diminution, presumably because the amorphous layer of Er doping with a few nanometers in thickness is too soft to sustain such forces. This behavior is very different from that of other foreign element-doped nanostructures.

From the above discussion, the core−shell structure in this case has little connection with the enhanced phase stability in Er-doped Ge nanowires. Therefore, we have to adopt other mechanism(s) to account for this phenomenon. In general, at ambient conditions, the different phases of a given material stay at different energy levels, so the phase transition can take place only when the energy intake either through compression or heating is high enough to overcome the energy barriers between two different phases. Ab initio method has been used to address the questions regarding the effects of interstitial O, N, and C on...
the $\alpha \rightarrow \omega$ transition in titanium.$^{15}$ The computation revealed that the presence of impurities in titanium based alloys suppresses the $\alpha \rightarrow \omega$ transformation by increasing the energy of $\omega$ phase relative to $\alpha$ phase and thus the energy barrier itself. The increased energy difference in turn shifts the $\alpha \rightarrow \omega$ phase boundary upward by several gigapascals and thus increases the stability of $\alpha$ phase at room temperature. However, we have to be cautious to use this rationale to explain Er-doped Ge nanowires, because, unlike the titanium alloys, the Er atoms were predominantly doped onto the surface of Ge nanowires, so the doped Er atoms do not significantly alter the material’s composition or lattice configuration in the interior bulk of Ge nanowires, but only its surface environment.

In general, the nanostructure has an expanded surface with populated defects, interfacial boundaries, and dangling bonds, which are energetically more favorable for nucleating the new phase under pressure. When a nanostructure is doped with exotic element(s) under high temperature, those doping atoms are more likely to pair with the dangling bonds and fill the interstice on the surface of the nanostructure. Therefore, the overall efficacy of surface doping is a lowering of the energy level of the nanostructure through surface modification and decoration, causing the elevation of the energy gap between the two phases. Considering that the previous study already revealed the highly concentrated dangling bonds on the surface of Ge nanowires,$^{7}$ it is conceivable to use the surface modification and decoration by Er dopants to explain the unique high pressure phenomenon observed in Er-doped Ge nanowires.

In the present case, the surface modification induced elevation of the energy barrier between cubic and $\beta$-Sn phase of Ge nanowires influences the phase transitions of cubic $\rightarrow$ $\beta$-Sn in the compression stage and $\beta$-Sn $\rightarrow$ cubic phase in the decompression stage. Such impact increases the phase stability of cubic phase with a higher onset transition pressure (13.0 GPa) during compression and of $\beta$-Sn phase with a lower onset pressure (4.3 GPa) during decompression when compared to the observations in undoped Ge nanowires under identical test conditions.

Besides its effect on the onset phase transition pressure, the Er-doping has a distinct effect on the kinetics of phase transformation, defined as the pressure span required for a complete phase transition. In undoped Ge nanowires, the transformation completes within the pressure span of approximate 7.1 GPa, while it is about 3.5 GPa in Er-doped nanowires. The smaller pressure span in Er-doped Ge nanowires suggests that Er impurity centers do enhance the kinetic driving force for the phase transition. This, thus, facilitates the nucleation and growth of $\beta$-Sn phase with the consumption of the original cubic phase in a more rapid manner.

### CONCLUSIONS

In summary, phase transitions of undoped and Er-doped Ge nanowires with a diameter of ∼50 nm were investigated under high pressures by using in situ synchrotron XRD and Raman spectroscopy in a diamond anvil cell. Under high pressure, undoped Ge nanowires start transforming to $\beta$-Sn structure at a pressure around 9.6 GPa, which is lower than that observed in bulk Ge. This discrepancy can be explained from a misfit in strain energy, in the sense that the smaller misfit in Ge nanowires would stimulate the phase transformation to a lower pressure. The Er dopants play a critical role in the phase transition of Ge by showing a higher onset transition pressure and smaller pressure span needed for a complete cubic $\rightarrow$ $\beta$-Sn phase transition in Er-doped Ge nanowires. During the decompression stage, the $\beta$-Sn phase shows an increased stability in Er-doped Ge nanowires. The enhanced phase stability is due to the surface-doping induced, enlarged energy difference or energy gap between the two phases. In contrast, the surface doping does not influence the change in lattice parameters of Ge nanowires under pressures. This study may provide a new method to design, control, and improve the phase stability and thus the performance of semiconductors.

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**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

Portions of this work were performed at HPCAT (Sector 16), Advanced Photon Source (APS), Argonne National Laboratory. HPCAT operations are supported by DOE-NNSA under Award No. DE-NA0001974, with partial instrumentation funding by NSF. This research used resources of the APS, a DOE Office of Science User Facility operated for the DOE Office of Science by ANL under Contract No. DE-AC02-06CH11357. Y.W. is grateful to the Research Faculty Fellowship of Oakland University for supporting this research. J.L.C. acknowledges the Robert A. Welch Foundation (Grant P-1212) for financial support of this research.

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