Supplementary information for Physical chemistry Chemical Physics

Abnormal elastic modulus behavior in a crystalline-amorphous core-shell nanowire system

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Fig. S1 Schematic illustration of the sample preparation. (a) Dispensing the InAs NWs on the AAO membrane. (b-c) Transferring a single InAs NW by using the tungsten tip. (d) Placing the InAs NW on the PTP and fixing the InAs NW with epoxy. (e) Performing atomic layer deposition.
**Supplementary information S2: Atomic structure of InAs NW before and after ALD**

In this study, the atomic layer deposition of Al$_2$O$_3$ was performed at a working temperature of 70 °C, which is not high enough temperature to change the crystalline property and the phase of InAs NW \(^1,^2\). We proved this assumption by comparing the HR-TEM images and the selected-area electron diffraction (SAED) patterns of InAs NW and InAs/Al$_2$O$_3$ core-shell NWs. According to Fig. S2, the stacking fault on the \{111\} plane, represented by the strong streaks in SAED patterns, were still present in InAs/Al$_2$O$_3$ core-shell NWs. In addition, the relative positions of the diffraction spots in the inset in Fig. S2 b are same as those in the inset in Fig.S2 a, which indicates that the crystalline property of the InAs surrounded by Al$_2$O$_3$ layers, e.g. symmetry and lattice constant, is same as that of pristine InAs NW. Because the atomic and electronic structure of InAs NW did not change during the Al$_2$O$_3$ coating, the elastic modulus of InAs NW is constant regardless of the shell existence.

According to the previous studies, the interfacial oxide such as In-oxide and As-oxide were formed between InAs NW and Al$_2$O$_3$ shell during the Al$_2$O$_3$ deposition \(^3\). However, the thickness of those oxide layer was almost 0.8 nm, containing 0.5 nm of In-oxide and 0.3 nm of As-oxide. Although the elastic modulus of interfacial oxide (i.e., 145 GPa for In-oxide) \(^4\) are obviously different from that of InAs (i.e., 79 GPa), the area ratio of In-oxide and As-oxide layer to the total InAs NW is less than 5%. Therefore, the formation of interfacial oxide during the Al$_2$O$_3$ coating does not play a role to change the elastic modulus of InAs NW.

![Fig. S2 HR-TEM image of (a) InAs NW and (b) InAs/amorphous Al$_2$O$_3$ (20 nm) core-shell. The stacking faults were formed along the <111> directions. The inset is the corresponding selected-area electron diffraction (SAED) pattern.](image-url)

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Supplementary information S3: The comparison between $E_s$ at the shell thickness of 20 and 40 nm

The measured $E_s$ of 20 nm-thick shell is ~ 0.2 GPa (i.e., average) larger than that of 40 nm-thick shell. Although this gap is smaller than the corresponding value of predicted elastic modulus, obtained by Eq.2 (~ 4 GPa), the errors between measured and predicted elastic modulus at the shell thickness of 20 nm and 40 nm are 2.2 % and 1.2 %, respectively. We concluded that these error values are reasonable when considering the uncertainty of measurement. (see Fig. S3)

![Fig. S3 The comparison of predicted $E_s$ and experimental $E_s$ in the shell thickness range from 20 nm to 40 nm](image-url)
Supplementary information S4: BOE etching time vs. Shell thickness

Fig. S4 (a) Thickness of the Al₂O₃ against the BOE etching time.
Supplementary information S5: Electron energy loss spectroscopy measurement in Al$_2$O$_3$ shell

In order to explain a difference of structural features between inner and outer region of the shell, we performed the electron energy loss spectroscopy (EELS) experiment. EEL spectra was obtained by using FEI Titan cube G3 80-300 S/TEM. The FEI Titan cube G3 80-300 was equipped with double Cs correctors and Gatan image filter Quantum ER (Gatan, Inc). The EELS experiment was performed at 120 keV to minimize the electron beam damage. The camera length was 115 mm, the collection angle was 14.37 mrad, and dispersion was 0.1 eV/channel. The EEL spectra were obtained from two regions in the amorphous Al$_2$O$_3$ shell where ~20 nm (inner site) and ~70 nm (outer site) from the InAs NW/a-Al$_2$O$_3$ interface, respectively. The EELS experiment was performed after the in-situ tensile test. (see Fig. S5a).

The result was shown in Fig. S5b. The overall shape of the Al 2p edge in the inner shell (~20 nm from the interface) is similar to that of $\alpha$-Al$_2$O$_3$ crystalline phase $^{1,2}$, indicating that the bonding characteristics of amorphous Al$_2$O$_3$ and the $\alpha$-Al$_2$O$_3$ phase are close to each other. However, the shape of Al 2p edge is significantly changed in the outer shell; the intensity of the peak at ~80 eV decreased compared to that of inner shell, the peak at ~100 eV shifts to lower energy by ~2 eV. In addition, the pre-edge shoulder was observed at ~73 eV in the outer shell, which is absent in the inner shell (the onset of the Al 2p edge is at ~75.7 eV in the inner shell). A similar pre-edge shoulder can be observed in the $\gamma$-Al$_2$O$_3$ crystalline phase $^{1,2}$, where 4-coordinated (tetrahedral) Al site exist, which indicate that the outer shell of the amorphous Al$_2$O$_3$ contains a tetrahedrally bonded Al feature. Note that the $\alpha$-Al$_2$O$_3$ crystalline phase contains only 6-coordinated (octahedral) Al $^{1,2}$. Based on the EELS data, we expect that the bonding characteristics of inner and outer shell of amorphous Al$_2$O$_3$ are similar to that of $\alpha$-like Al$_2$O$_3$ and $\gamma$-like Al$_2$O$_3$ crystalline phases, respectively.
Fig. S5 (a) EELS measurement position in amorphous Al$_2$O$_3$ shell, (b) The average EELS measurements, Al L$_{2,3}$-edge, at two different thicknesses (i.e., ~20 nm - inner site and 70 nm – outer site). The spectra is background subtracted.


Supplementary information S6: Atomic layer deposition characteristics

(a)

![Graph showing thickness of Al₂O₃ against ALD cycle number.](image)

(b)

![Graph showing growth rate of Al₂O₃ as a function of Al₂O₃ thickness.](image)

Fig. S6 (a) Thickness of the Al₂O₃ against the number of ALD cycles. (b) Growth rate of Al₂O₃ as a function of deposition thickness.