The microstructure origin of large strain plastically deformed SiC nanowires

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Abstract. Surprisingly large strain plasticity has been demonstrated for ceramic SiC nanowires through in-situ deformation experiments near room temperature. This article reports a detailed electron energy-loss spectroscopy (EELS) study of deformation-induced localized plastic zones in a bent SiC nanowire. Both the “red shift” of the plasmon peak and the characteristic fine structure at Si L-edge absorption are consistent with local amorphisation of SiC. The recorded C K-edge fine structure is processed to remove the contribution from the surface amorphous carbon and the extracted C K-edge fine structure has no characteristic sp2-related pre-edge peak and hence is also consistent with amorphous SiC. These results suggest that the large strain plasticity in SiC nanowires is enabled by crystalline-to-amorphous transition.

1. Introduction
Traditionally, large strain plasticity can be found in bulk metals or alloys but it is quite rare in ceramic materials especially at low temperature (~300K). With the reduction in dimensionality, we expect nanomaterials to exhibit unusual and novel properties such as high hardness and high strength [1-3]. More recently, surprisingly large strain plasticity has been demonstrated for ceramic SiC nanowires through in-situ deformation experiments near room temperature [4]. Figure 1 shows the transmission electron micrographs of typical morphologies of (a) the elastic and (b) the subsequent plastic bends in a deformed SiC nanowire (NW) respectively. The electron diffraction analysis at the plastic deformed region of the bending SiC NW suggests that this plastic bending deformation may have induced a local amorphisation. But the electron diffraction can not give material specific information about microstructure at atomic level. With its high energy and spatial resolution, EELS can be used not only for qualitative and quantitative elemental analysis but also for microstructure determination. We therefore have applied this technique to investigate the atomic structure of these deformed SiC regions in order to understand the origin of this nanoscale plasticity.
2. Experimental results of EELS
EELS experiments have been performed in a JEM-2010F transmission electron microscope equipped with a Gatan Enfina PEELS system operating at 200 kV. The nanowire bending experiment and diffraction analysis have been carried out in situ as reported in ref. [4]. Figure 2 shows one of the Si L$_{2,3}$-edge spectra from different positions in the deformed region. For comparison, we have also plotted the corresponding Si L$_{2,3}$-edge spectra for crystalline 6H-SiC [5] and electron beam amorphous SiC [5] carried out both above and below the room temperature (RT). Figure 3 shows the corresponding C K-edge spectra, one from the centre and the other from the rim of the deformed region of the nanowire. Unfortunately, large variation is observed and can be attributed to carbon contamination. Figure 4 shows the corresponding spatially resolved low loss spectra and the difference between those from the rim and the centre of the nanowire is again obvious.

3. Discussions
Si L$_{2,3}$-edge spectra should give us important clues as the fine structure is not likely to be affected by the carbon contamination. The comparison of the Si L$_{2,3}$-edge absorption spectra shown in Figure 2 suggests that the deformed SiC is spectroscopically closer to the amorphous SiC than to the crystalline SiC, except for the small peak at 158 eV. For this reason, it is important that we get independent information from an analysis of the low loss and the C K-edge spectra.
In EELS the first 100eV is often called the low-loss region. Within this region, the main energy-loss mechanism involves excitation of the outer-shell electrons. A plasmon model can describe this excitation process reasonably well [6]. The understanding of the plasmon response from the rim of the SiC NW needs to take into account the surface response of the nanowire which is complicated by carbon contamination. However, the plasmon energy deduced from spectra taken near the centre of the nanowire is position independent [Figure 4 (a) and (b)], suggesting that it is not affected by the surface condition of the nanowire. As the diameter of the nanowire is about 40 nm, we can assume that only the bulk plasmon is excited for the beam passing through near the centre of the nanowire.

The ‘bulk plasmon energy’ can be expressed [6] as $E_p = \hbar \sqrt{\frac{n e^2}{\varepsilon_0 m_0}}$, where $n$ represents the number of valence electrons per unit volume, $e$ the electronic charge, $m_0$ the rest mass of the electron and $\varepsilon_0$ the vacuum dielectric permittivity. The 0.6 eV ‘red shift’ of the plasma peak at the deformed region of the bending SiC NW relative to the undeformed region as shown in Figure 4 (c) demonstrates a reduction in the valence electron density, or the corresponding atomic density, at the deformed region relative to the undeformed region. This suggests that the bending deformation induced a volume expansion of the SiC NWs. Similarly this ‘red shift’ in bulk plasmon excitation has also been observed in amorphous SiC induced by intense electron irradiation [5].

To interpret the C K-edge spectra, we need to separate out the contribution of the carbon contamination from the intrinsic contribution of the deformed region. Quantitative EELS elemental analysis at sampling point 2 (S2 in Figure 5 (a)) indicated that the silicon to carbon atomic ratio is 0.53 ± 0.075. Assuming the parity in the atomic contents of silicon and carbon for SiC, we can deduce that the recorded C K-edge fine structure at S2 involves about 53% intrinsic contribution from the deformed region, the additional 47% is the contribution from the surface carbon contamination. The same analysis at sampling point 1(S1 in Figure 5 (a)) suggests that it has a negligible SiC contribution.

We therefore normalize both spectra and use the spectrum taken from S1 as the reference for the carbon contamination and subtract away the desired fraction of it from the normalized spectrum taken from S2. The result of the subtraction indicates that when 47% surface carbon contamination has been subtracted away from the original C K-edge [Figure 5 (b)] the 285 eV shoulder characteristic of $sp^2$ bonding totally disappears because the second derivative becomes positive. This processed result indicates that the intrinsic C K-edge fine structure at the deformed region has no $sp^2$ bonding. Compared with the C K-edge from the amorphous SiC after $1.3 \times 10^{24}$ e/m²’s irradiation [5] [Figure 5

![Figure 4. (a) Spatially resolved low-loss spectrum image radially across the deformed region of a bending SiC NW. (b) The plasmon energy at the different position of the deformed region. (c) Plasmon-loss spectra taken from the deformed region and from the undeformed region.](image-url)
the fine structure in the processed result shows a broad similarity with that from the electron beam induced amorphous phase. However, minor differences such as the different curvatures of the two spectra in the 290-310 eV energy range are observed, indicating a possible difference in the atomic structure of the two different amorphous structures.

\[\text{Figure 5. (a) C K-edge fine structure taken from two sampling points S1 and S2 whose locations are shown in the insert. (b) The second derivative of the fractional subtraction of the normalized spectrum taken from S1 from that taken from S2. (c) The comparison of the C K-edge fine structure from the deformed region (with carbon contamination contribution removed) and that from amorphous SiC [5] (A) after above RT irradiation and (B) after below RT irradiation.} \]

Although electron irradiation can induce SiC amorphisation, it is generally carried out using MeV electrons and with a dose much larger than that used in our analysis [5]. In our case, the energy of the incident electron beam is only 200KeV. Nevertheless, we have also checked the irradiation effect experimentally by acquiring spectra under the identical condition from the undeformed region. As the results shown in Figure 3 and 4, they are consistent with the crystalline SiC. More importantly, no time dependent feature has been observed, except for those from the carbon contamination. These results indicate that the amorphisation at the plastically deformed regions of the bending SiC NWs is induced by strain. However, its structural characteristics, particularly with respect to the electron irradiation induced amorphous phase, need to be further investigated.

4. Summary

The comprehensive EELS analysis identified that the deformed regions of the bending SiC NWs have been amorphourised. The result suggests that the large strain plasticity in SiC NWs is enabled by crystalline-to-amorphous transition which involves a volume expansion.

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