We demonstrate that surface stresses in epitaxially grown VO$_2$ nanowires (NWs) have a strong effect on the appearance and stability of intermediate insulating M$_2$ phases, as well as the spatial distribution of insulating and metallic domains during structural phase transitions. During the transition from an insulating M$_1$ phase to a metallic R phase, the coexistence of insulating M$_1$ and M$_2$ phases with the absence of a metallic R phase was observed at atmospheric pressure (See Figure 1). In addition, we show that for a VO$_2$ NW without the presence of an epitaxial interface, surface stresses dominantly lead to spatially inhomogeneous phase transitions between insulating and metallic phases. In contrast, for a VO$_2$ NW with the presence of an epitaxial interface, the strong epitaxial interface interaction leads to additional stresses resulting in uniformly alternating insulating and metallic domains along the NW length. In order to demonstrate the detailed structural changes and coexistence of two different insulating phases (M$_1$, M$_2$), we prepared naturally bent NWs with uniform local curvature and non-clamped (strain-free interface) on a c-cut sapphire substrate using a PDMS transfer method, which is a technique widely used for transferring graphene. Raman measurements were carried out at two featured positions; i) the non-clamped, straight part of a NW (A in the upper inset of Figure 4a), and ii) the largest bent part of a NW with the high tensile strain at the centre of the outer edge of the local curvature region (B in the lower inset of Figure 2a). As shown in Figure 2a, the evolution of Raman spectra obtained from the straight region of a NW (A), which exhibits direct structural changes from M$_1$ to M$_2$ phases, is quite similar to that measured on a transferred NW non-clamped shown in Figure 1. Interestingly, in the bent part of a NW (B), coexistence of both M$_1$ and M$_2$ phases as evidenced by peaks associated with only M$_1$ and M$_2$ phases were observed even at room temperature. As the temperature increases, the intensity of M$_1$ peaks gradually decreases and that of M$_2$ peaks continuously increases, showing the evolution of M$_1$-M$_2$ phases. When the temperature increases further, R phases start to appear.

References

Figure 1. Temperature dependence of Raman spectra of transferred individual VO$_2$ NWs. As the temperature increases, phonon frequencies shift toward higher frequencies and phase transitions from an M$_1$ to an R phase occur spatially along the NW length. Raman spectra indicated by A, B and C were obtained from the circle region of the NWs, respectively (left inset). Optical images of bright and dark domain patterns corresponding to insulating and metallic phases, respectively (right inset), reveal spatial phase transitions along the NW length.

Figure 2. (a) Raman spectra obtained from the straight part (A in the upper inset) and bent part (B in the lower inset) of a VO$_2$ NW, which show the direct evolution of M$_1$-M$_2$ phases. (b) Temperature dependence of XRD data from ensembles of epitaxially grown VO$_2$ NWs, measured during cooling from 303 K to 6 K. These results demonstrate that M$_1$ and M$_2$ phases can coexist with the absence of an R phase at atmospheric pressure.