EFFECT OF VACANCIES ON THE ULTIMATE TENSILE STRAIN OF ZnO NANOWIRES

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Summary The Influences of lateral dimension and vacancy on the tensile behaviour of ZnO nanowires are assessed using molecular dynamics simulations. These results show that ultimate tensile strain reduces dramatically as vacancies concentration increases, which is much more pronounced than effect of lateral dimension. The influence of the positions of vacancies is also discussed. This work provides a better understanding on the large scatter of ultimate tensile strain observed in experiments.

INTRODUCTION

ZnO nanostructures have important potential applications in nano-size optical, electronic, sensor and electromechanical devices [1]. The functioning of devices requires components to either retain necessary structures or assume alternate structures under specific external loadings. The mechanical properties such as the Young's modulus and tensile strength of ZnO nanowires (NWs) with different diameters have been measured using various experimental techniques [2]. Some of the results show significant size effects on Young's modulus and strength, while others do not. This paradox can partly be attributed to differences in experimental platforms and measurement methods. However, the variation in measured data is so large (e.g. scatter in measured ultimate tensile strength in some cases is over 50% [3]) that it can even obscure the effect of NW size. In addition to the accuracy of experimental measurement, vacancies in the material may also account for part of the scattering in measured properties. So far, there is still a lack of understanding on how vacancies affect properties and how large their contributions are. It is hard to quantify influence of vacancies by experiments. In this regard, atomistic simulations provide an important mean-complement. In this paper, molecular dynamics (MD) simulations are performed to investigate the influence of lateral dimension and vacancies on the tensile response of [0001]-oriented ZnO NWs. The analysis accounts for changes in both density and positions of vacancies. The focus is on atomistic rearrangement near vacancies, structural transformation, and the variations in ultimate tensile strain as the wires size and vacancies are changed.

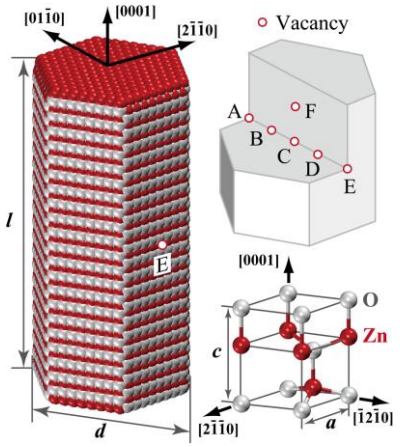

Figure 1. ZnO nanowire with the wurtzite structure and vacancies.

RESULTS AND DISCUSSIONS

Size dependence

Experiments and computations [2] have revealed size effects on Young's modulus and fracture strengths of ZnO NWs. To establish a standard for comparison, 5 defect-free NWs with diameters ranging from 2.93 to 5.53 nm are analysed first (Figure 1). Similar to the findings of Wang et al. [4], a stress-induced phase transformation from the original wurtzite (WZ) structure to the tetragonal structure (TS) is observed. This transformation leads to a precipitous drop in stress (B→C in Figure 2). As the wire diameter increases from 2.93 to 5.53 nm, the Young's modulus decreases 10.24% from 205 to 184 GPa for the WZ phase. Furthermore, the ultimate tensile strain (UTS) of the WZ phase changes 6.73% from 6.65×10^{-2} to 7.13×10^{-2}. Theoretically, the size effect is strongly related to the nanostructure surfaces and becomes weak with the decreasing surface-to-volume ratio as structure size increases [5]. However, it has been reported that the measured UTS data were remarkably scattered over 50% for NWs with diameter of about 40 nm [6]. The simulation results (UTS fluctuates with 6.73% as diameter differs by 1.89 times) reveal that dimensional uncertainty is not the only factor or perhaps not even a major one that causes the large scatter of UTS measured from experiments.

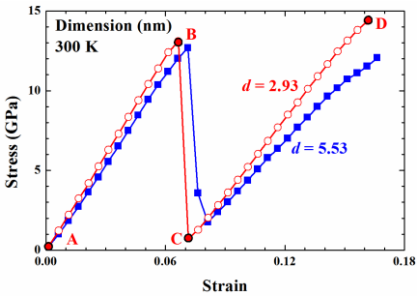

Figure 2. Tensile stress-strain curves of ZnO NWs with diameters of 2.93 nm (open circles) and 5.53 nm (solid squares).

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Effect of vacancy on strength

The stress-strain curves of wires (d = 4.88 nm) with different vacancy densities are shown in Figure 3. The UTS substantially decreases by 43.25% from 6.89×10^{-2} to 3.91×10^{-2} as the vacancy density increases from 0 to 4.93×10^{19} cm^{-3}. However, the Young's modulus only changes slightly (approximately 2.83%). Therefore, the UTS is much more sensitive to the presence of vacancies than Young's modulus does. It is important to point out that the large variation in UTS over this range of vacancies in terms of percentage is comparable to that observed in experiments (about 50%). The variation in UTS caused by vacancies is much larger than the variation caused by size change and easily account for the large scatter in data from experiments. In most experiments, the presence of vacancies was neither controlled nor characterized. It is therefore not surprising that some experiments show size-dependent fracture strains while others appear to suggest no size dependence.

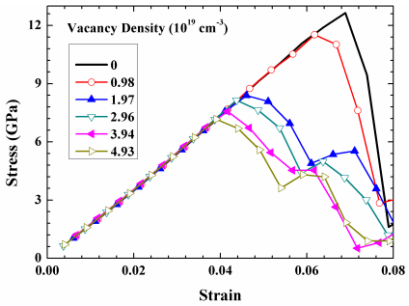

Figure 3. Tensile stress-strain relations of ZnO NWs (d = 4.88 nm) with diverse vacancy densities.

To analyse how vacancies interact with each other and how the arrangement of vacancies affects the response of a NW, two cases are considered. Both consist of a pair of vacancies, with one pair parallel (denoted as V-type, points C and F in Figure 1) and the other perpendicular (denoted as H-type, points B and D in Figure 1) to the c-axis of the WZ structure (also the axis of the NW). The H-type vacancies pair reduces the UTS by approximately 10.9% and the V-type vacancies reduce the UTS by 3.3%. Microstructural analysis reveals that this discrepancy results from different propagating modes of the TS structure from the vacancies (as shown in Figure 4). Specifically, the TS structure propagates along the wire axis first and only grows transversely after it has propagated through the length of the wire. The width of TS zone in V-type wire is one lattice unit. However, in H-type wire, the width becomes double, which allows the transformation to proceed at a higher rate and causes a lower UTS in contrast to that of the V-type wire.

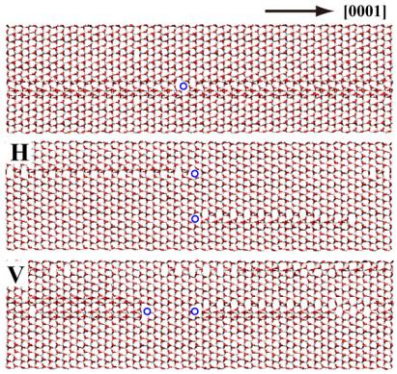

Figure 4. TS structure initiating and propagating from vacancies during tensile loading

In nanostructures, the surface stress due to high surface-to-volume ratios is another important factor that affects physical, chemical and mechanical properties. To ascertain this surface effect, NWs with a pair of Zn and O vacancies (interior, point C in Figure 1) and (surface, point E in Figure 1) are considered. In contrast to a perfect wire without vacancies, a NW with surface vacancies loses 26.1% UTS (5.09×10^{-2} compared with 6.89×10^{-2}). This reduction is much prominent than that, 2.18%, of the case with interior vacancies.

CONCLUSTIONS

MD simulations are carried out to investigate the influence of vacancies on the tensile behavior of WZ-structured ZnO NWs. As lateral dimension increases from 2.93 to 5.53 nm, the UTS varies from 6.65×10^{-2} to 7.13×10^{-2}, with a fluctuation of 6.7%. However, behaviours of ZnO NWs with vacancies show that vacancies can significantly reduce the UTS. When the interior vacancy concentration increases from 0 to 4.93×10^{19} cm^{-3}, the UTS decreases by 43%, which is comparable to the range of data scatter, about 50%, observed in experiments. Vacancies serve as nucleation sites of the WZ-to-TS structure transformation which significantly weaken the strength and UTS of ZnO NWs. The positions and arrangements of vacancies also have prominent influence on UTS. In particular, vacancy pairs perpendicular to wire axis are more detrimental to the strength and UTS than pairs parallel to the axis. Similarly, vacancies located on the surface of a ZnO NW induce substantial reduction in strength and UTS in comparing with that caused by interior vacancies.

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