Materials Physics and Mechanics 24 (2015) 403-409 Received: November 13, 2015

CHARACTERIZATION OF STRAIN-INDUCED STRUCTURAL TRANSFORMATIONS IN CdSe NANOWIRES USING MOLECULAR DYNAMICS SIMULATION

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Abstract. In this work, we have successfully applied the method of molecular dynamics simulation to simulate structural transformations in CdSe nanowire when subjected to a tensile deformation along the <001> direction. The time evolution of atomic configuration and the energy of deformation were calculated. These quantities clearly revealed four distinct structural transformations that take place during the tensile deformation, namely: the quasi-elastic, plastic, flow and fracture. Our results indicate that the deformation process starts with the appearance of vacancies, Frenkel pairs and interstitial atoms, after which atomic displacement, dislocation, anti-phase boundary and grain boundary formation take place before slipping and alloy fracture.

1. Introduction

Nano materials play an essential rule in modern life technological applications. They are coming into use in health care, electronics, cosmetics and other areas of nanotechnology. As a broad definition, they are defined as materials with at least one external dimension is in the size range from approximately 1-100 nanometers. Some of them are classified as nanoparticles, nanotubes and nanowires.

Of special interest are the nanowires (one-dimensional solids). Nanowires are structures that have a lateral size constrained to tens of nanometers or less and an unconstrained longitudinal size. They are incredibly thin structures that have an incredible length-to-width ratio. Due to their unique length scale, they exhibit superior electrical and mechanical properties and other length scale dependent phenomena. Nowadays, they have emerging applications in several fields, including energy, environment, electronics, and even in cosmetics. Currently, they are considered as potential materials for future nano scale sensors and actuators.

Nanowires have had great impact on different technological aspects. For example, very recently, graphene coated with zinc oxide nanowires have had emerging applications in solar cells technology [1, 2], as they enabled the production of competitive low cost and flexible solar cells at high enough efficiency. In addition, light absorbing nanowires embedded in a flexible polymer film is another method being developed to produce low cost flexible solar panels. Furthermore, cadmium sulfide nanowires coated with copper sulfide have been used in making inexpensive solar cells [3, 4]. In the environmental sector, silver chloride nanowires have been used as a photocatalysis to decompose organic molecules in polluted

water. Similarly, using an electrified filter composed of silver nanowires, carbon nanotubes and cotton have been used to kill bacteria in water. In the electronic sector, nanowires have been used in making transistors without P-N junction, as well as electrodes used in flat-panel displays. This enabled the flat-panels to be flexible and thinner than current flat-panel displays.

2. Mechanical Properties of Nanowires

Mechanical properties of nanowires have been studied extensively because of the unique mechanical response of such structures as a building block [5]. Some nanostructures exhibit the superior mechanical properties such as elastic modulus and/or fracture stress to those of bulk materials [6]. Hence, many nanowires have been used instead of their bulk counterparts for their improved mechanical properties. For example, using silicon nanowires, instead of bulk silicon fixes the problem of the silicon cracking that has been seen on electrodes made up of bulk silicon.

Wu et al. [7] using atomic force microscopy, have studied the mechanical properties of ultrahigh-strength gold nanowires. They reported that for Au nanowires, Young's modulus is essentially independent of diameter, whereas the yield strength is largest for the smallest diameter wires, with strengths up to 100 times that of bulk materials, and substantially larger than that reported for bulk nano crystalline metals.

In contrast to bulk nano crystalline metals, nanowire plasticity is characterized by strain-hardening, demonstrating that dislocation motion and pile-up are still operative down to diameters of 40 nm [7].

Feng et al. [8] have studied the mechanical properties of nanowires using nano indentation. On the other hand, Wang et al. [9] using transmission electron microscopy have studied the mechanical properties of silicon carbide-silica biaxial nanowires, and their structural transformation between a biaxial and coaxial configuration. The origin of such remarkable properties of some nanostructures is still unclear. Aish et al. [10 - 13] have showed that the mechanical properties of Ni nanowires are highly dependent on the size, shape as well as the atomic vacancies in the nanowire.

3. CdSe Nanowires:

CdSe nanowires are of great technological interest. They have potential applications in photoelectrical and photovoltaics [14]. They have been successfully synthesized by using various methods including electrochemistry, solution chemical reactions, and self-catalysis thermal evaporation [15]. CdSe nanowires have been used in single-electron transistors [16, 17], electrochromic [18], charge-coupling devices [19], biomolecular labeling [20], and light-emitting diodes [21]. Very recently, CdSe nanoribbons have been used in photodetectors and field-effect transistors (FETs) [22, 23].

Mechanical characterization of CdSe nanowires is quite essential for deep understanding of their functionality as well as for the possibility of modeling and engineering new useful materials based on them.

Aiming at understanding the mechanical properties of CdSe nanowires, we have applied molecular dynamics simulation to characterize structural transformations that take place in the wire when subjected to uniaxial stress.

4. Molecular Dynamics Simulation

Molecular dynamics (MD) simulation was originally conceived within theoretical physics in the late 1950s [24, 25]. It is a computer simulation of physical movements of atoms and molecules. The atoms and molecules are allowed to interact for a period of time, giving a view of the motion of the atoms. In the most common MD simulations, the trajectories of

atoms and molecules are determined by numerically solving Newton's equations of motion for the system of interacting particles, where forces among the particles and potential energies are defined by interatomic potentials or molecular mechanics force fields [26, 27].

Molecular dynamics simulations have been applied successfully in many fields including chemical physics, materials science and in the modeling process of biomolecules. Comprehensive reviews of the subject can be found in literature [28 - 31].

5. Mathematical Model

In this work, molecular dynamics using Morse pair potential [32] is used to simulate the dynamics of the atomic structure of CdSe nanowire when subjected to a uniaxial tension at 300 K. The Morse pair potential energy function is of the form:

$$V(r) = D_e(1-e^{-a(r-r_e)})^2. \tag{1}$$

Here r is the distance between the atoms, r_e is the equilibrium bond distance, D_e is the depth of the potential well (defined relative to the dissociated atoms), and a is a parameter that controls the 'width' of the potential (the smaller a is, the larger the well).

Similar to the Lennard-Jones potential [33], Morse pair potential is a combination of a short-range repulsion term and a long-range attraction term. Thus, for a given two atoms i and j, Morse pair potential (Φ_{ij}) between them is given by:

$$\Phi_{ij}(r) = D_{ij}\beta_{ij}e^{-\alpha_{ij}r}[\beta_{ij}e^{-\alpha_{ij}r} - 2]. \tag{2}$$

Here α_{ij}, β_{ij} and D_{ij} are parameters defining the interaction of pairs of atoms of type i and j and r is the radial distance between the two atoms. Here the interaction among the atoms is assumed to be dependent only on the interatomic distances. Consequently, when considering a closed system, the force acting on the i^{th} atom, will be:

$$F = -\sum_{i=1, i\neq j}^{N}\sum_{j=1}^{N}\frac{d\varphi_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)}{d(r_i - r_j)}. \tag{3}$$

The cut off interaction radius among atoms was set to extend up to till the third nearest neighbor distance. This cut off distance was tested and found to be suitable as the interaction beyond this distance is very negligible. The potential energy term (E) of a system of N atoms is given by:

$$E = \frac{1}{2}\sum_{i=1, i\neq j}^{N}\sum_{j=1}^{N}\varphi_{ij}(|\mathbf{r}_i - \mathbf{r}_j|), \tag{4}$$

where $\mathbf{r}_i$ is the radius vector of the i^{th} atom.

Mathematically, molecular dynamics method [34, 35] describes a set of ordinary differential equations of motion. In solving these equations, we have used numerical Euler method with half-step [36]. The absolute values of the initial velocities of the atoms ($|v_i|$) in the cell were calculated using the formula:

$$|v_i| = \sqrt{\frac{2K_BT}{m_i}}, \tag{5}$$

where K_B is the Boltzmann's constant, T is the temperature and m_i is the mass of atom of type i.

In the current study, a nanowire of CdSe alloy was simulated as a rectangular parallelepiped of dimensions 4.235 nm × 4.781 nm × 6.961 nm. This corresponds to a packing of 24 atoms along the side in the basis of the rectangular parallelepiped and 36 atoms along its height, resulting in 10368 atoms. Free boundary conditions were applied to the calculated cell along the <010> and <001> directions and rigid boundary conditions along the <100> direction.

The interactions among different pairs of atoms in the CdSe alloy were assumed to be given by Morse pair potentials with the parameters used in [32]. In these calculations, and since the directions of the velocities of the atoms were set randomly, the total momentum of the entire computational cell adds up to zero. The ordering and restructuring processes of the atoms involved in the current MD simulation were based on redistribution rates in accordance with Maxwell's probability distribution law.

The current MD simulation is performed at 300 K, which was maintained and adjusted every 10-13 Sec. Here the temperature was kept constant via the direct velocity scaling method [37].

After full relaxation, extension strain loading was applied by uniformly scaling the Z coordinates. The atoms at each end of the nanowire were constrained, and could displace only along the Z direction during each loading step. The stepwise tensile strain is 0.02. It was relaxed for some time in each step. Both the strain step and relaxation time determine the strain rate.

In this simulation, the following parameters were monitored: the stored energy of deformation, diffusion coefficients of the components in the different directions, the overall diffusion coefficient, kinetic and potential energy of the crystal.

6. Results and Discussion

During the uniaxial deformation applied to the nanowire along the <001> direction, the reserved (stored) energy of deformation per atom was calculated as a function of time (duration of stress application) and is plotted in Fig. 1.

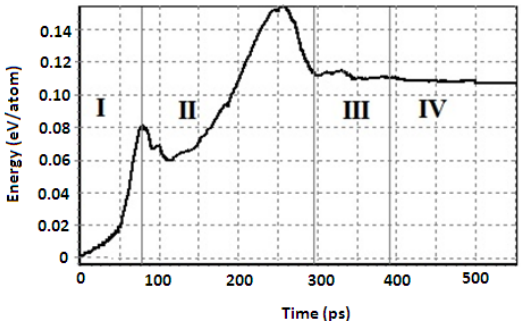

Fig. 1. The time evolution of the stored energy per atom (energy of deformation) in CdSe nanowire when subjected to a tensile deformation along the <001> direction**.**

Figure 1 reveals four distinct structural features that manifest structural and energy transformations, namely: the quasi-elastic deformation, plastic deformation, flow (necking) and fracture. These transformations are marked in Fig. 1 as I, II, III and IV, respectively.

During the initial stage (quasi-elastic deformation), small displacements of atoms occur and the defects are not observed. The stored energy during this stage varies according to a parabolic law. It comes to end at the point of energy bifurcation.

Differences among atomic layers along the <001> direction have been observed at the first stage indicating a consecutive splitting of the family of atomic planes in {001} into monatomic ones. This splitting takes place in the central part of the nanowire more intensively as shown in Fig. 2.

At the end of the first stage of splitting, the deformation of {001} plane was observed near rigid captures that led to the formation of a crack on the boundary of the section between absolutely rigid captures and the calculated block of the alloy.

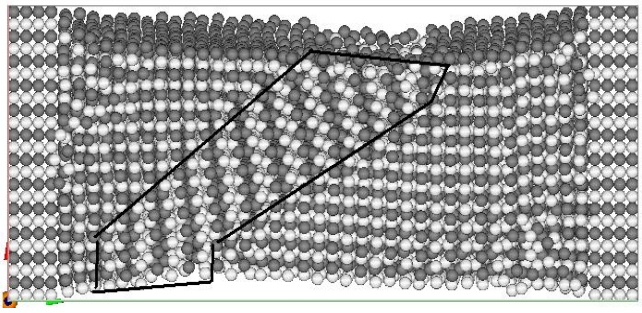

Fig. 2. The formation of a domain in the central portion of the CdSe nanowire at 60 ps along the <001> direction.

The significant atomic displacements were determined near the captures at the end of the first deformation stage. The tension at captures reached 12 GPa.
By the end of stage II, the formation of a "neck" is observed, as indicated by Fig. 3.

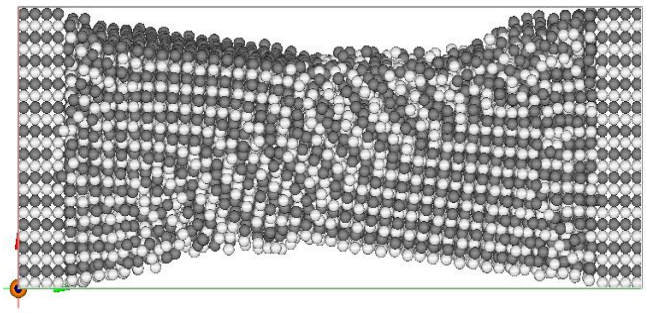

Fig. 3. Atomic configuration during the second stage of deformation (100 ps) in the CdSe nanowire along the <001> direction. The formation of a "neck" is observed.

During the third stage (early break) restructuring is primarily near the "neck" as shown in Fig. 4, which is reflected in the change of the stored energy (Fig. 1).

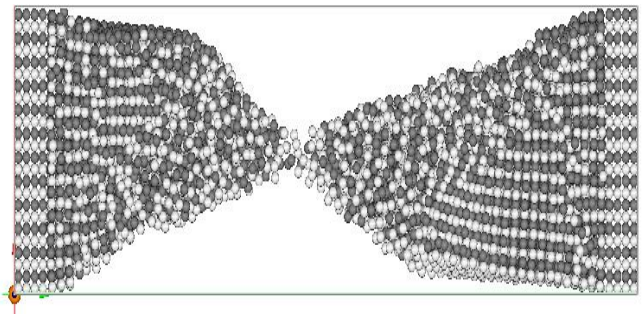

Fig. 4. Atomic configuration of the CdSe nanowire at 320 ps (the third stage of deformation).

Figure 5 shows a schematic representation of the nanowire deformation process when subjected to a uniaxial tension. It is evident that the deformation process starts with the appearance of atomic domains where the atoms in each domain displace collectively towards some preferred directions.

The current investigation shows the heterogeneity of plastic deformation of CdSe nanowire. It is evident that this deformation starts to occur at the central area of the wire. It is

found that structural elements in each domain depend on the orientation of the axis of compression. Moreover, the anisotropy of structural changes taking place in CdSe nanowire does depend on its orientation. In particular, the development of plastic deformation stages in the direction <001> produces the formation of anti-phase boundaries and C-domains. C-domains form in the second stage of deformation.

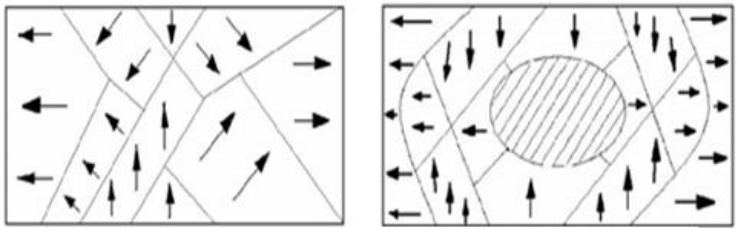

Fig. 5. The appearance of structural domains where the atoms in each domain move collectively towards preferred directions (a) on the surface of the nanowire and (b) at the core.

7. Conclusions

Dynamics of structural changes in CdSe nanowires when subjected to a uniaxial tension at 300 K have been studied using molecular dynamics simulation. Atomic configurations and strain energy have been characterized during stress application. These quantities revealed four distinct structural transformations that take place during tensile deformation, namely: the quasi-elastic, plastic, flow and fracture.

These transformations are characterized by distinct structural features as manifested by the strain energy curve and the appearance of structural defects.

The first stage of deformation is characterized by the formation of a sliding on the substructure of CdSe nanowire, as manifested by the rotation of the central portion of the alloy. It was found that the features of structural and energy transformations for non-cubic symmetry of the alloy in the second stage of deformation depend on the orientation of the axis of tension. The third stage is characterized by the formation of a neck, where the stored strain energy in that stage varied only slightly. In the fourth stage of deformation the nanowire is separated into two segments, there is a sliding with the formation of a neck at the center of deformed nanowire.

In this work, we have shown that the deformation process starts with the appearance of vacancies, Frenkel pairs and interstitial atoms, after which atomic displacement, dislocation, anti-phase boundary and grain boundary formation take place before slipping and alloy fracture. The nature of this uniaxial tensile deformation corresponds to brittle fracture at low temperatures.

Acknowledgment

M.M. Aish and M.D. Starostenkov would like to acknowledge support from the Ministry of Education and Science of the Russian Federation, Project No. 166 of program "Formation of state tasks to higher education institutions in terms of science research" and from RFBR, research projects No. 14-08-90416 Ukr_a and No. 15-48-04127 r_sibir_a.

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