Physics Letters A 381 (2017) 1568–1572

Contents lists available at ScienceDirect

Physics Letters A

www.elsevier.com/locate/pla

Edge eigen-stress and eigen-displacement of armchair molybdenum disulfide nanoribbons

Quan Wu [a], Xi Li [a], Alex A. Volinsky [b], Yanjing Su [a,*]

[a] Corrosion and Protection Center, Key Laboratory for Environmental Fracture (MOE), University of Science and Technology Beijing, Beijing 100083, China
[b] Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

ARTICLE INFO

Article history:
Received 19 September 2016
Received in revised form 23 February 2017
Accepted 6 March 2017
Available online 9 March 2017
Communicated by R. Wu

Keywords:
MoS_2 nanoribbons
Size-dependent
Young's modulus
Poisson's ratio

ABSTRACT

Edge effects on mechanical properties of armchair molybdenum disulfide nanoribbons were investigated using first principles calculations. The edge eigen-stress model was applied to explain the relaxation process of forming molybdenum disulfide nanoribbon. Edge effects on surface atoms fluctuation degree were obtained from each fully relaxed nanoribbon with different width. Changes of the relaxed armchair molybdenum disulfide nanoribbons structure can be expressed using hexagonal perimeters pattern. Based on the thickness change, relaxed armchair molybdenum disulfide nanoribbons tensile/compression tests were simulated, providing intrinsic edge elastic parameters, such as eigen-stress, Young's modulus and Poisson's ratio.

1. Introduction

Molybdenum disulfide (MoS_2) belongs to two-dimensional (2D) transition metal dichalcogenides [1]. Single layer MoS_2 is constructed by graphene-like hexagonal arrangement of Mo and S atoms stacked together to form S–Mo–S sandwiches. Recently, single layer MoS_2 captured researchers' interest due to its prominent mechanical [2–4], electronic [5], thermal [6], and optoelectronic [7] properties.

MoS_2 nanoribbons (MoS_2 NRs) are MoS_2 strips with ultra-narrow width, obtained using electrochemical methods [8]. Based on their edge configuration, MoS_2 NRs are classified as armchair MoS_2 nanoribbons ($AMoS_2$ NRs) and zigzag MoS_2 nanoribbons ($ZMoS_2$ NRs). For armchair graphene ribbons (AGNRs), unique mechanical properties were found where AGNRs exhibited three periodicities in the nominal Young's modulus and Poisson's ratio [25]. Considering their band gap [9], intrinsic carrier mobility [10] and binding energy [11], $AMoS_2$ NRs exhibit oscillating width-dependent behavior. The authors wanted to figure out whether $AMoS_2$Rs exhibit three periodicities in the nominal Young's modulus and Poisson's ratio, and further investigate the reasons. The elastic modulus [10–12], edge energy density [13,14] and edge stress [13,15] have been obtained for MoS_2 NRs considered as 2D structures, i.e., without taking into account the influence of MoS_2 NRs thickness. However, the thickness of MoS_2 NRs varies with the width change. Hence, it is important to accurately determine the edge properties by taking into consideration the thickness change. Intrinsic edge parameters effects on mechanical properties, surface atoms fluctuation degree, edge eigen-stress and Poisson's ratio need to be investigated.

By taking the stress-free monolayer MoS_2 sheet as a reference, an $AMoS_2$ NR can be created from it. A newly formed $AMoS_2$ NR, with the lattice constant of the stress-free monolayer MoS_2 sheet, has substantially higher excess energy, and the free-edges (S–Mo–S sandwich structure) of the $AMoS_2$ NR are formed with eigen-stress [16]. The newly formed $AMoS_2$ NR relaxes unavoidably to reduce the excess energy and the edge eigen-stress. This relaxation causes initial deformation and relaxation-induced strain in the $AMoS_2$ NR along the length and thickness directions.

In the present study, $AMoS_2$ NRs were allowed to relax in two steps of normal relaxation and parallel relaxation, so that the change in the excess energy could be systematically studied. The surface atoms fluctuation degree was obtained from the changes of atomic positions at two layers of sulfur atoms. Perimeters of each hexagon ring in the relaxed $AMoS_2$ NRs are given to investigate the structure change. The nominal Young's modulus and Poisson's ratio were determined by performing tensile/compressive tests on the relaxed $AMoS_2$ NRs to extract the edge eigen-stress, edge Young's modulus and Poisson's ratio.

* Corresponding author.
E-mail addresses: volinsky@usf.edu (A.A. Volinsky), yjsu@ustb.edu.cn (Y. Su).

http://dx.doi.org/10.1016/j.physleta.2017.03.002
0375-9601/

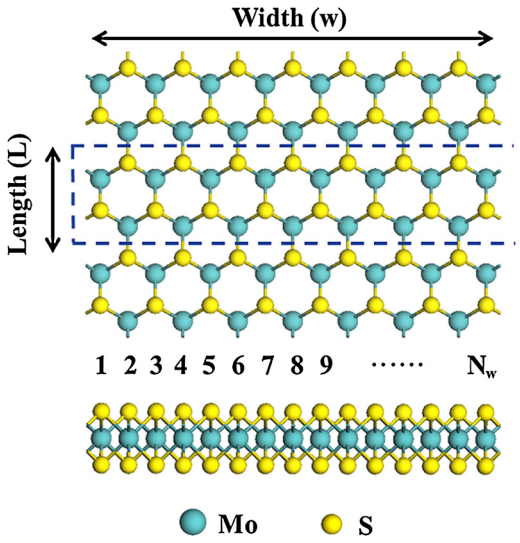

Fig. 1. The calculated geometry of the $AMoS_2$ NRs.

2. Computational methods

Density functional theory (DFT) calculations were performed by using the Vienna *ab* initio simulation package (VASP) [17] with the project-augmented wave (PAW) method [18]. The exchange correlation interaction was treated by the generalized gradient approximation with the PW91 functional [19]. The PAW potentials were used with the $4p^6 5s^1 4d^5$ valence states of molybdenum atoms and the $3s^2 3p^4$ valence states of sulfur atoms. The $11 \times 11 \times 1$ and $1 \times 11 \times 1$ Monkhorst–Pack [20] k-points were set for the monolayer MoS_2 and $AMoS_2$ NRs, respectively, with an energy cut-off of 550 eV. The accuracy of the total energy calculations was on the order of 0.1 meV.

The equilibrium configuration of the monolayer MoS_2 was determined by energy minimization. The spacing of the nearest Mo–Mo was 3.197 Å, the bond length of the Mo–S bond was 2.421 Å, while the distance between the top and bottom layers in single layer MoS_2 was 3.132 Å, in good agreement with previous reports [21,22]. When an $AMoS_2$ NR is removed from its stress-free parent sheet, it has original dimensions of $L_0 \times W_0 \times T_0$, where L_0, W_0 and T_0 represent the length, width and thickness of the $AMoS_2$ NR without any relaxation, respectively. The unrelaxed $AMoS_2$ NRs width W_0 was determined by using the equal mass method [23], i.e., the total mass of the atoms in the $AMoS_2$ NR was set equal to the product of the monolayer MoS_2 density and the volume of the simulated representative nanoribbon in its undistorted configuration. The number of atoms across the ribbon width index N_w was adopted to represent the width in this study, and the calculated $AMoS_2$ NR width ranged from 1.3 nm to 2.4 nm. The unrelaxed $AMoS_2$ NRs thickness T_0 was equal to the thickness of the MoS_2 monolayer, assumed to be 0.65 nm [3]. Fig. 1 shows that the structure was treated with periodic boundary conditions along the $AMoS_2$ NR length. To eliminate the interaction between $AMoS_2$ NRs, the calculated structure contained two 20 Å thick vacuum layers along the width and thickness directions.

3. Theoretical analysis

The relaxation process of $AMoS_2$ NR was separated into normal and parallel relaxations [16,25]. In the normal relaxation, all of the atoms were allowed to move in width and thickness directions, whereas in parallel relaxation, all of the atoms were allowed to move in all three directions.

The dimensions changes to $L^{ini} \times W^{ini} \times T^{ini}$ with $L^{ini} = L_0 + \Delta L$, $W^{ini} = W_0 + 2p_0 + \Delta W$ and $T^{ini} = T_0 + \Delta T$, where p_0 is the edge eigen-displacement [22] and the change of width ΔW and thickness ΔT are caused by the Poisson's ratio effect. Relaxation causes initial deformation, and the relaxation-induced strain along the $AMoS_2$ NRs length and thickness directions are called the initial strain. The initial strain along the length and thickness directions is calculated as $\varepsilon_L^{ini} = (L^{ini} - L_0)/L_0$ and $\varepsilon_T^{ini} = (T^{ini} - T_0)/T_0$.

In equilibrium, zero total force along the length direction must be satisfied along any lateral section perpendicular to the length, and the traction-free boundary conditions must be met along the $AMoS_2$ NR edges. The initial edge stress and core stress after parallel relaxation were calculated as $\sigma_e^{ini} = \sigma_0^{ini} + Y_e \varepsilon_L^{ini}$ and $\sigma_c^{ini} = Y_c \varepsilon_L^{ini}$, respectively. The self-balanced force requires

$$2F_e^{ini} + F_c^{ini} = 0 \tag{1}$$

where $F_e^{ini} = T^{ini}\sigma_e^{ini} = T^{ini}(\sigma_0^{ini} + Y_e\varepsilon_L^{ini})$ and $F_c^{ini} = W^{ini}T^{ini}Y_c\varepsilon_L^{ini}$ denotes the edge force and the core force, which includes the surface force of the two surfaces (S atomic layer) and the core force (Mo atomic layer) per unit length, respectively.

4. Results and discussion

Fig. 2(b) shows that the initial strain along the length direction increases as the width increases, whereas the initial strain along the thickness direction decreases with the width. As the dimensions change, the structures also change.

The edge effect on surface atoms fluctuation degree R_a of each fully relaxed $AMoS_2$ NR with different width was proposed to reflect the fluctuations of sulfur atomic layers at zero temperature. It was calculated using $Ra = \frac{1}{n_s}\sum_{i=1}^{n_s/2}[|Z_{top}^{NR} - Z_{top}^{sheet}| + |Z_{bottom}^{NR} - Z_{bottom}^{sheet}|]$, where n_s is the total number of sulfur atoms in $AMoS_2$ NRs, Z_{top}^{NR}, Z_{bottom}^{NR}, Z_{top}^{sheet} and Z_{bottom}^{sheet} denote the sulfur atomic coordinate value along the thickness direction of the $AMoS_2$ NR's top-layer, $AMoS_2$ NR's bottom-layer, sheet's top-layer, and sheet's bottom-layer, respectively. Fig. 2(a) shows that the $AMoS_2$ NR surface atoms fluctuation degree increases as the width decreases. In this case, the change of thickness ΔT is determined by $\Delta T = d_{S-S}^{NR} - d_{S-S}^{sheet}$ in consideration of the uneven surface, where d_{S-S}^{NR} and d_{S-S}^{sheet} denote the arithmetic mean distance between the top layer and the bottom layer in $AMoS_2$ NRs and stress-free MoS_2 parent sheet, respectively.

The latest study [25] shows that the armchair graphene nanoribbons (AG NRs) with similar honeycomb-like structure to $AMoS_2$ NRs exhibit three periodicities in the nominal Young's modulus and Poisson's ratio. Investigations of the Young's modulus and Poisson's ratio of $AMoS_2$ NRs are reported later in the paper. The phenomenon of the width-dependent elastic properties and perimeter patterns with a periodicity of three depends on the nature of the edge, which can be explained by the Clar sextets [26]. The Clar sextets defined as six π-electrons localized in a single hexagons ring separated from adjacent rings by the C–C single bonds. Corresponding relationships were found between the hexagon perimeters pattern and the Clar sextets in AG NRs [26]. Without the Clar sextets, $AMoS_2$ NRs exhibit different hexagon perimeters pattern. Fig. 3 shows the hexagon "perimeters" (six sides are not in the same plane) of each relaxed $AMoS_2$ NRs with width N_w ranging from 8 to 15. In contrast to the AG NRs, the perimeter patterns of the $AMoS_2$ NRs show different variation rules. For the $AMoS_2$ NRs with $3n+1$ and $3n-1$ width, no obvious arrangement rule was observed. According to the structural symmetry, $AMoS_2$ NRs were classified by central ($N_w = 2k$) and mirror ($N_w = 2k+1$) symmetry. As the width increases, the value of the hexagonal perimeter approaches the infinite MoS_2 sheet value.