

# Study of Electronic Transport Properties of Atomic Wires (Al & Pt) on MoS<sub>2</sub> Monolayers

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We have investigated the structural and electronic transport properties of metallic monoatomic wires sandwiched on the MoS<sub>2</sub> monolayer are investigated within the density functional theory (DFT). The anchoring of the atomic wires on the semiconducting monolayer significantly modifies its electronic properties; the metallic characteristics of the assembled monolayers appear in the density of states (DOS) and band structure of the system. We find that Al wires induce the so-called n-type doping effect, whereas Pt wires induce a p-type doping effect in the monolayer. The distinctly different behavior of Pt–MoS<sub>2</sub> compared to the Al metallic wires is reflected in the calculated current–voltage characteristics of the assembled monolayers with a highly asymmetric behavior of the out-of-the-plane tunneling current with respect to the polarity of the external bias. The results of the present study are likely to extend the functionality of the MoS<sub>2</sub> monolayer as a candidate material for the novel applications in the areas of catalysis and optoelectronic devices.

**Keywords:** Aluminum Atomicwires, Platinum Atomicwires, Structural Stability, Density of States, Molybdenum Disulfide (MoS<sub>2</sub>) Monolayer.

## 1. INTRODUCTION

Monoatomic wires have been investigated theoretically in a large number of studies. two-dimensional molybdenum disulfide (MoS<sub>2</sub>) has received considerable attention<sup>1-4</sup> since its synthesis has been carried out by the exfoliation technique<sup>5</sup> similar to the one applied to graphene. Under ambient conditions, the bulk MoS<sub>2</sub> has a hexagonal structure with the space group of P63/mmc,<sup>6</sup> in which a layer of Mo atoms is sandwiched between two layers of S atoms. This atomic trilayer configuration is referred as a monolayer.<sup>7</sup> The atoms within the MoS<sub>2</sub> monolayer are covalently bonded, whereas individual atomic sheets are bonded via weak van der Waals force. Although the bulk MoS<sub>2</sub> is a semiconductor with an indirect gap, the monolayer has a direct gap.<sup>8</sup> The monolayers of MoS<sub>2</sub> have versatile and tunable properties,<sup>9-11</sup> which are useful for their applications in nanoelectronics.<sup>12</sup> They also complement graphene in applications which require thin transparent semiconductors and are expected to have excellent gas sensing performance due to high surface-to-volume ratio.<sup>13</sup> The fabrication of electronic devices for next-generation applications generally requires a combination of conducting and insulating materials, using which higher performance and greater flexibility can be achieved.<sup>14-16</sup> For example, Al nanowires deposited on graphene led to significant enhancement in the conductivity of the functionalized graphene. Consequently, the Al–graphene system has a greater potential in the high performance, flexible energy conversion and storage devices. Considering these experimental results, we are intrigued by the role played by the metallic nanostructures in modifying the electronic properties of a monolayer substrate. Does the effect solely come from nanostructures or does the interfacial chemistry of the nanostructure with monolayer play a dominant role? Specifically, we will focus on the monoatomic wires of Al and Pt anchored on the MoS<sub>2</sub> monolayer and on the calculation of their stability and electronic properties using the density function theory (DFT). Note that the metallic monoatomic wires, including Al and Pt, have been synthesized in the break-junction experiments and on the substrate.<sup>17,18</sup> The results of the present study are expected to extend the functionality of the MoS<sub>2</sub> monolayer as a candidate material for the novel applications in the areas of catalysis and optoelectronic devices.

## 2. COMPUTATIONAL DETAILS

The calculations have been performed using norm-conserving, relativistic pseudopotentials<sup>19</sup> as implemented in the SIESTA program package<sup>20</sup> were used in a fully separable non-local Kleinman and Bylander form to treat electron–ion interactions. The Kohn–Sham orbitals were expanded in a linear combination of numerical pseudoatomic orbitals using split-valance double-zeta with polarization (DZP) basis sets for all atoms. Electronic structure calculations were performed within the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) parameterization of the exchange and correlation functional form. The MoS<sub>2</sub> monolayer, atomic wire and wire–monolayer systems were simulated in the xy plane using the supercell approximation and periodic boundary conditions. A vacuum distance of 15 Å along the z-direction was used to ensure negligible interactions between 2D system images. All calculated equilibrium configurations are fully relaxed, with residual forces smaller than 0.01 eV Å<sup>-1</sup>.

## 3. CALCULATIONS AND RESULTS

First of all, we have calculated the lattice constant is 3.23 Å, for the pristine MoS<sub>2</sub> monolayer, and the values for the Mo–S bond length and S–Mo–S bond angle are 2.47 Å and 82°, respectively. These GGA-PBE values are in complete agreement with the previously reported calculations on the pristine monolayer.<sup>8</sup> Note that the structural configuration of the MoS<sub>2</sub> monolayer shows the location of each Mo atom at the center of a trigonal prismatic cage formed by six S atoms. The calculated lattice constants of the monoatomic linear wires of Al and Pt are 2.55 and 2.45 Å, respectively. Employing the projected augmented wave (PAW) method, the GGA-PBE values were previously reported as 2.65 and 2.23 Å for Al and Pt monoatomic wires, respectively.<sup>21</sup> A difference of about 5% in the value of the lattice constant of Pt may be due to the nature of pseudopotentials used in the PAW method because in our study, the norm-conserving, relativistic pseudopotentials were used to represent the core orbitals for Pt. Moreover, Pt is different from the other noble metal wires considered in terms of the valance electronic configuration, which may have different dependence of pseudopotential parameters in theoretical methods, such as the choice of cut-off radius, choice of semicore states and nonlinear exchange correlation correction for the interaction of core–valence electrons.

**Table 1.** The calculated (average) distance between wire and monolayer ( $R_{\text{wire-layer}}$ ), and the binding energy ( $E_b$ ) of the assembled monolayer

| System              | $R_{\text{wire-layer}}$ (Å) | Hollow site | Top site |
|---------------------|-----------------------------|-------------|----------|
| Al–MoS <sub>2</sub> | 2.5                         | 0.16        | 0.14     |
| Pt–MoS <sub>2</sub> | 2.2                         | 0.36        | 0.53     |

Due to a lattice mismatch between the monolayer and monoatomic wires (Table 1), we need to minimize the strain at the interface by the suitable choice of a supercell simulating the assembled monolayer. The alignment of atomic wires deposited on the surface of the MoS<sub>2</sub> monolayer can be considered via either the top or hollow sites; the former refers to the case where the metal atoms are directly on top of the S atoms, and the latter refers to the case where the metal atoms are positioned between the two S atoms, thus directly above the underlying Mo atoms of the monolayer (Fig. 1). The preferred binding site was determined by calculating the total energy of the assembled monolayer by varying separation between the wire and the monolayer for both the top and hollow sites. The binding energy of the assembled system is defined with respect to the constituent components as  $E_b = (E_{\text{MoS}_2} + E_{\text{wire}}) - (E_{\text{wire/MoS}_2})$ . A positive value of  $E_b$  indicates the stability of the assembled system. The calculated results are listed in Table 1, which shows that the difference in the  $E_b$  of the hollow and top sites for Al is small, although the hollow site is slightly preferred over the top site (0.02 eV). On the other hand, Pt certainly prefers the top site of the MoS<sub>2</sub> monolayer. The predicted order of stability at the top site is Pt > Al for the assembled monolayers. Interestingly, calculations performed at the GGA-PBE level of theory on the diatomic molecules evaluate the binding energy/per atom as 2.35, and 2.12 eV for PtS, and AlS molecules, respectively. Therefore, the nature of bonding at the molecular level appears to persist for the wire–monolayer system.

## 4. CONCLUSIONS

The present study of the structural stability and electronic transport properties of the metallic monoatomic wires anchored on the MoS<sub>2</sub> monolayer are investigated. The calculated results show the stability of the assembled monolayers with Al and Pt wires. The electronic band structure and the density of states of the assembled monolayers reveal that states associated with metallic atomic wires appear in the vicinity of Fermi level, forming electron conduction channels. Al–MoS<sub>2</sub> systems are found to possess 2G<sub>0</sub> quantum ballistic conductance, while Pt–MoS<sub>2</sub> possesses 4G<sub>0</sub> quantum conductance due to partially filled Pt-d states. The transverse current calculated for the assembled monolayers in the STM-like setup show significantly enhanced conduction relative to the MoS<sub>2</sub> pristine monolayer. Asymmetric current–voltage characteristics are predicted for the assembled monolayers except Pt–MoS<sub>2</sub> for which, a distinctly different nature of bonding is seen at the interface of the assembled monolayer. Our results unambiguously find the interaction of the MoS<sub>2</sub> monolayer with the metallic monoatomic wires to be relatively strong, modifying its electronic properties. Al wires induce an n-type doping effect, whereas Pt wire induces a p-type doping effect in the MoS<sub>2</sub> monolayer. The predicted interactions and doping effects of the monoatomic wires can be verified by various techniques, e.g. Raman spectra which can reflect changes in the electronic structure of the monolayer induced by metal wires. We believe that the results of the present study are likely to extend the functionality of the MoS<sub>2</sub> monolayer as a candidate material for the novel applications in the areas of catalysis and optoelectronic devices. It is well known that the catalytic activity is generally attributed to the unsaturated sites or excess charge on the surface of the nanomaterial. In the case of the MoS<sub>2</sub> monolayer, our results show that each of the S atoms have a charge of 0.3 e in excess, and the interaction of metal wires further induce n- or p-type doping effects in the pristine monolayer. Therefore, we believe that the interaction of metallic wires on MoS<sub>2</sub> is expected to enhance the catalytic activity, particularly in the hydrodesulfurization process.

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