Materials and Design 160 (2018) 371–376

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Direct fabrication of graphite-mica heterojunction and *in situ* control of their relative orientation

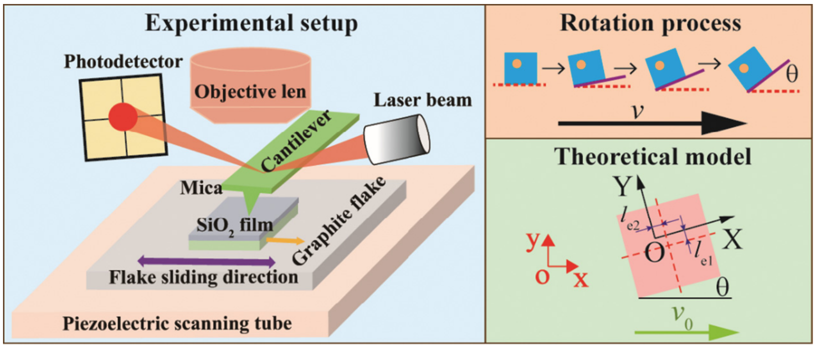
Bingtong Liu [a,b], Jin Wang [c,d], Xiaona Peng [a,b], Cangyu Qu [c,d], Ming Ma [a,b,c,*], Quanshui Zheng [b,c,d]

[a] *Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China*
[b] *State Key Laboratory of Tribology, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China*
[c] *Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, China*
[d] *Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China*

HIGHLIGHTS

- A monocrystalline van der Waals junction is constructed by transferring a microscale graphite flake onto a mica substrate.
- A method to control the relative orientation between the surfaces both dynamically and quantitatively is developed.
- A parameter-free theoretical model is developed, showing good agreement with experimental observations quantitatively.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 August 2018
Received in revised form 14 September 2018
Accepted 15 September 2018
Available online 17 September 2018

Keywords:
Graphite
Mica
Relative orientation
Heterojunction

ABSTRACT

In this paper, we directly construct monocrystalline van der Waals heterojunctions by transferring microscale graphite flakes onto millimeter-sized muscovite mica surfaces. The relative orientation between the surfaces is controlled by sliding the graphite flakes with elaborate manipulation. Experimentally the rotation angle of the flake is found to increase with sliding duration and eccentricity. A parameter-free theoretical model is developed, showing good agreement with experimental observations quantitatively. Our results can not only be used to control the frictional and electrical properties of van der Waals heterojunctions *via* their relative orientation, but also provide a new way in distinguishing friction resulted from edges or from the in-plane interactions.

1. Introduction

Van der Waals (vdW) heterojunctions have attracted great attention due to their novel mechanical [1,2] and electrical [3–5] properties, which have been extensively applied in sensors [6,7], flexible photovoltaic devices [8,9] and *etc.* Devices with interfaces composed of vdW heterojunctions with ultralow friction have been regarded as a promising approach to reduce friction and wear. This is of particular importance for mechanical systems such as Micro-Electro-Mechanical-Systems (MEMS) [10]. The superior frictional properties are attributed to the structural superlubricity at interfaces [11], a fascinating tribological phenomenon where the lateral interactions between two incommensurate contacting surfaces effectively cancel each other out, resulting in ultra-low sliding friction.

---

* Corresponding author at: State Key Laboratory of Tribology, Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China.
E-mail address: maming16@tsinghua.edu.cn (M. Ma).

https://doi.org/10.1016/j.matdes.2018.09.032

Structural superlubricity has been found in many systems at the nanoscale or microscale, such as graphite/graphite [11,12], graphite/*h*-BN [13,14] and metal clusters on graphite [15–17]. Although an abundant of works has been done, it still remains further researches on the robust superlubricity at microscale. About the scale-up of the system, there are a few limiting factors, with the lack of large-scale monocrystalline surfaces being the critical one. To this end, we notice that graphite and muscovite mica are good candidates. As found in the self-retraction experiments, monocrystalline graphite shows the microscale structural superlubricity [12,18,19]. Muscovite mica ($KAl_2(Al,Si_3)O_{10}(OH)_2$) has also been known for its feasibility in generating an atomically smooth surface on millimeter scale [20]. Thus, it would be interesting to find out whether heterojunctions composed of these two materials can be used as potential systems for superlubricity.

The other key issue for superlubricity is the robustness against the relative orientation at the interface. With the friction being ultralow, small perturbations such as the tip or thermal fluctuations could cause rotation between the two contacting surfaces, resulting in a high friction state [13,14,21–23]. Until now, the relative orientation is typically controlled by tip-driving [22,24,25], thermal fluctuation [21,22] or precise rotation during transfer process [26,27]. However, simple tip-driving is usually insufficient to control the orientation quantitatively [22]. An effective tip-driving method is recently reported but restricted to a certain geometry of the systems [3,24]. Thermally induced rotation is limited to samples with size up to hundreds of nanometers [21] and is not dynamically rotatable. The same limitation also holds for controlling the orientation with precise transfer process, though the size of the systems could be larger [27]. Thus, it is of great significance to develop a simple and quantitative method to control the relative orientation between surfaces dynamically.

In this paper, we report a direct method to construct monocrystalline graphite-mica heterojunctions by transferring a microscale graphite flake onto a millimeter-sized mica. For such a heterojunction, sliding the graphite flake against the mica substrate with an eccentric tip could result in a relative rotation of the flake. The rotation angle can be controlled by tuning the sliding duration/distance and eccentricity with Atomic Force Microscope (AFM). This enables us to control the relative orientation of the heterojunction both quantitatively and dynamically. A parameter-free theoretical model which describes the dependence of the rotation angle on the sliding distance and eccentricity is proposed, showing good agreements with the experiments. In this model, the friction resulted from the edges and the in-plane interactions contribute differently to the rotation. By fitting the measured rotation angle to the model, it is possible to estimate the contributions of friction from the in-plane interactions and the edges.

2. Experiment

2.1. Fabrication of the graphite – mica heterojunction

The heterojunction is constructed by transferring the upper part of a graphite mesa onto a muscovite mica surface. As shown in Fig. 1, we first select a graphite mesa with Self-Retraction Motion (SRM) using a tungsten tip with the tip radius of curvature less than 3 μm, mounted on a micromanipulator (Kleindiek, MM3A-EM), to shear the graphite flake by pressing the SiO_2 cap. When the upper flake of the mesa is sheared out, some flakes can retract back to their initial positions after the tip is released. This SRM behavior happens due to the fact that the system always tends to reduce its surface free energy, and the friction between the upper and lower part of the mesa is extremely low, *i.e.* being superlubric [12,13]. Careful characterizations show that the interface for graphite mesa with SRM is atomically flat and monocrystalline [12,13], as detailed in Supplementary Note 1. The upper part of SRM graphite mesa is then attached to a tungsten tip and transferred onto the substrate, which is the basal (001) plane of a muscovite mica, after being freshly cleaved under ambient conditions. Because the adhesion force between a graphite flake and a mica is typically larger than that between a graphite flake and a tungsten tip, such transferring process can be easily done. The whole process is carried out under an optical microscope (Germany, Zeiss) [12].

Raman spectroscopy characterization of the graphite is performed on the surface of SRM graphite substrate. The low I_D/I_G ratio and the absence of D peak clearly show that the SRM graphite flake is almost defect-free (detailed in Supplementary Note 1). The morphology of the SRM graphite flake and mica is measured using White Light Interferometer (WLI) and AFM (NT-MDT, Russia). The WLI results show that the height fluctuation of the $42 \times 42\ \mu m^2$ mica is less than 2 nm. Due to the limited performance of the lateral resolution of WLI, these flat surfaces are further characterized by AFM. The height images as shown in Fig. 2a and e verify that the surfaces are flat and clean. This enables us to construct an interface with close contact between them due to the vdW interaction and the normal pressure applied. More detailed information of the fabrication and characterization process can be found in Supplementary Note 1.

The atomic structures of the SRM graphite surface (Fig. 2a–d) and air-cleaved mica (Fig. 2e–h) surface are examined using AFM (Oxford, Cypher-ES), as shown in Fig. 2. Nine regions on each surface are chosen respectively. The hexagonal periodic structures are clearly shown in Fig. 2c and g. To characterize the atomic lattice orientation quantitatively, taking the graphite surface as an example, for each region shown in Fig. 2a, the filtered images are fitted to five snow-like patterns (Fig. 2c). The standard deviation of the five fitted angles is calculated to be $\Delta\theta_{gr} = 1.27^\circ$. The lattice orientations of the 9 regions labeled in Fig. 2a

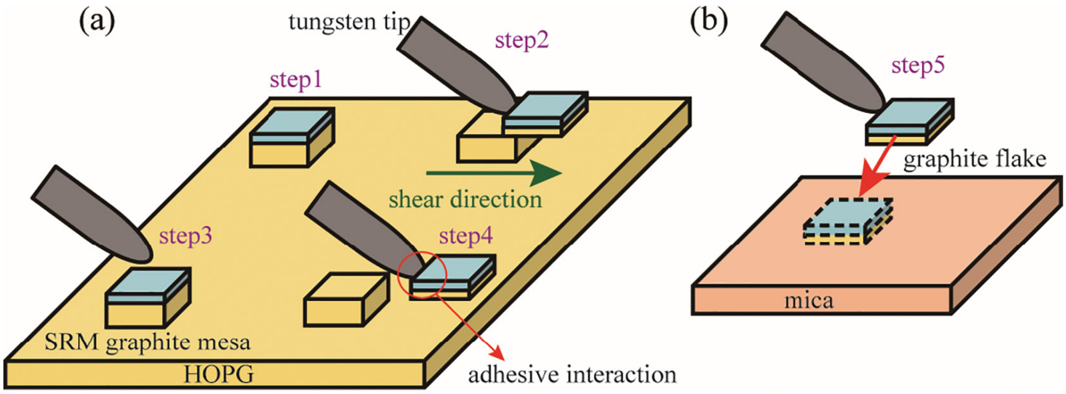


Fig. 1. Fabrication process of the graphite-mica heterojunction. (a) The selection of SRM graphite mesa and graphite flake, *i.e.* the upper part of the mesa. (b) The transferring process of SRM graphite flake to mica substrate. The typical size of the graphite mesa is $4 \times 4 \times 1\ \mu m^3$, and the thickness of the SiO_2 cap is about 200 nm.