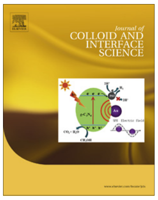
Journal of Colloid and Interface Science 505 (2017) 776–782

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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



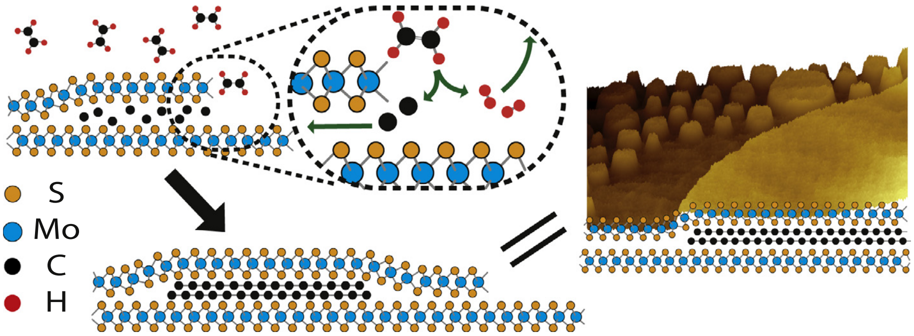
Regular Article

Chemical vapor deposition growth of bilayer graphene in between molybdenum disulfide sheets

Wojciech Kwieciñski [a,b,*], Kai Sotthewes [a], Bene Poelsema [a], Harold J.W. Zandvliet [a], Pantelis Bampoulis [a,c,*]

[a] Physics of Interfaces and Nanomaterials, MESA+Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands
[b] Faculty of Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland
[c] Physics of Fluids and J.M. Burgers Centre for Fluid Mechanics, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 3 April 2017
Revised 20 June 2017
Accepted 22 June 2017
Available online 23 June 2017

Keywords:
MoS_2
Graphene
2D materials
Chemical vapor deposition
Heterostructures

ABSTRACT

Direct growth of flat micrometer-sized bilayer graphene islands in between molybdenum disulfide sheets is achieved by chemical vapor deposition of ethylene at about 800 °C. The temperature assisted decomposition of ethylene takes place mainly at molybdenum disulfide step edges. The carbon atoms intercalate at this high temperature, and during the deposition process, through defects of the molybdenum disulfide surface such as steps and wrinkles. Post growth atomic force microscopy images reveal that circular flat graphene islands have grown at a high yield. They consist of two graphene layers stacked on top of each other with a total thickness of 0.74 nm. Our results demonstrate direct, simple and high yield growth of graphene/molybdenum disulfide heterostructures, which can be of high importance in future nanoelectronic and optoelectronic applications.

1. Introduction

Graphene (Gr), an sp^2 hybridized carbon layer, has received tremendous attention due to its exceptional electronic and mechanical properties [1–3]. The discovery of the unique properties of graphene has triggered the revival of interest in other two-dimensional (2D) crystals, such as hexagonal boron nitride (h-BN), and transition metal dichalcogenides like molybdenum disulfide (MoS_2) [4]. These 2D atomic crystals bear great promise for various applications [4–6]. An elegant way to exploit the intrinsic properties of 2D crystals is using combinations of alternating weakly bound layers of different 2D crystals (e.g., graphene, h-BN and MoS_2), thus forming the so-called van der Waals heterostructures[7–13].

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[*] Corresponding authors at: Physics of Interfaces and Nanomaterials, MESA+Institute for Nanotechnology, University of Twente, P.O.Box 217, 7500AE Enschede, The Netherlands.

E-mail addresses: w.kwiecinski@utwente.nl (W. Kwieciñski), p.bampoulis@utwente.nl (P. Bampoulis).

http://dx.doi.org/10.1016/j.jcis.2017.06.076
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Van der Waals heterostructures have attracted a lot of attention due to their promise for future electronics, catalysis and battery industry[7,14–16]. Their key properties arise from the fact that in heterostructures each material maintains its intrinsic electronic structure owing to the weak, van der Waals, interactions between adjacent layers. For instance, graphene grown or mechanically transferred on h-BN has been shown to preserve its pristine properties [17]. The mobility of the charge carriers of graphene grown on h-BN via the chemical vapor deposition (CVD) method reaches 20.000–30.000 $cm^2 V^{-1} s^{-1}$ at room temperature [18,19].

Stacking graphene and MoS_2 is of potential interest in nanoelectronics and optoelectronics due to the tunable band gap of MoS_2 and its indirect to direct band gap transition[20–25] and the excellent electronic properties of graphene [1–3]. Many devices based on MoS_2/graphene heterostructures have already been fabricated. Field-effect transistors with a few-layers thick MoS_2 channel and graphene as a source, drain and gate electrodes have been realized and show an on/off ratio of $\sim 10^6$. The gate electrode was isolated by a few layers of h-BN, creating a transistor entirely out of 2D material components [26]. Furthermore, single-layer MoS_2 has been used as a tunneling barrier in a vertical graphene/MoS_2/graphene heterostructure creating a field-effect transistor with on/off ratios up to 10^5 at room temperature [27]. The hole-current flowing through this device was almost entirely spin-polarized. Vertical heterostructures can be used as highly efficient photodetector and photocurrent generators, tunable with a back-gate [28]. In addition, the mechanical properties of 2D materials may enable the fabrication of flexible electronic devices and help to scale-down electronics in the vertical dimension.

Therefore, the fabrication of high quality and large-area heterostructures is of fundamental and technological interest. At this moment, van der Waals heterostructures are prepared by PMMA (poly(methyl methacrylate)) assisted transfer of a 2D crystal on top of another. The 2D crystals have to be prepared in advance either by mechanical exfoliation, chemical vapor deposition or liquid phase exfoliation [3,29,30]. The process is extremely complicated, challenging and it has a very low yield. It gives rise to structural complexities and uncertainties. For example, the mutual azimuthal orientation of the stacked layers is not well controlled and in most cases it is even completely random. Furthermore, contamination trapped between the interfaces during the transfer process can lead to charge inhomogeneities [31]. It is highly desirable to develop a reliable, high yield and simple method for the fabrication of van der Waals heterostructures. Recently, graphene has been epitaxially grown on h-BN, ZnO and ZnS substrates via templating chemical vapor deposition [18,19,32–35]. In addition, MoS_2/graphene has been grown by CVD [12], by a hydrothermal method[36] and by an in-situ catalytic process by heating a Mo-oleate complex coated on sodium sulfate particles [37].

Here we present the successful growth of micrometer-sized bilayer graphene in between MoS_2 sheets. The growth is achieved by decomposition of ethylene molecules at the highly reactive step edges of MoS_2. The resulting carbon atoms (or dimers) intercalate, through step edges or defects on the surface, between subsurface MoS_2 trilayers, where the nucleation and growth of circular graphene bilayers occur. Our work paves the way for the direct engineering of graphene/MoS_2 heterostructures suitable for fundamental research as well as device application.

2. Experimental methods

Freshly cleaved MoS_2 samples (5×10 mm^2) were mechanically fixed on a Si substrate. The MoS_2/Si assembly was then mounted on a sample holder. The samples were subsequently inserted into a high vacuum chamber with a base pressure of 4×10^{-8} mbar. Ethylene was used as the carbon precursor and its pressure during deposition was set to 1.1×10^{-5} mbar. The underlying Si substrate was used to anneal the MoS_2 substrate by direct current heating. The temperature of the Si substrate was set to 800 ± 20 °C and was calibrated using a pyrometer. The duration of the process varied between different experiments. After the deposition, the samples stayed in vacuum for at least 12 h during the cool down. The cooling was realized by switching off the current heating and letting the system approach room temperature. Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) measurements were subsequently performed in N_2 environment by continuously purging with N_2 gas. The samples were imaged using tapping mode atomic force microscopy with an Agilent 5100 (Agilent) and SSS-FMR probes (Nanosensors) with a nominal spring constant of 2.8 N/m and a resonance frequency of 75 kHz. Scanning Tunneling Microscopy (STM) and Spectroscopy (STS) were performed in N_2 environment with an UHV variable temperature AFM/STM (Beetle TM, RHK Technology), with chemically etched W tips. For the X-ray Photoelectron Spectroscopy (XPS) measurements a Quantera SXM (Physical Electronics) was used. The X-rays were Al Ka, monochromatic at 1486.6 eV with a beam size of 200 μm. XPS measurements were done at several different locations on the samples.

3. Results

Fig. 1a shows an AFM topographic image of a freshly cleaved MoS_2 surface. MoS_2 consists of stacked sulfur-molybdenum-sulphur tri-layers and the surface is smooth with a root mean square (RMS) roughness of about 45 pm and a low step density. After 5 min of CVD, parts of the surface are covered with circularly shaped flat layers with various radii, as shown in Fig. 1b. Regions with a high concentration of small islands as well as regions with a low number density of large islands have been observed, as shown in Fig. 1b and d. Their size distribution shows a large variation (see Fig. 1e). These structures were formed only after the MoS_2 surface was heated to elevated temperatures and exposed to ethylene and thus will be referred to as carbon-induced layers. Phase images obtained simultaneously with AFM topographic images reveal that there is no phase difference between the layers and the intrinsic MoS_2 surface. Fig. 1b shows an example of a topographic image and the corresponding phase image is given in Fig. 1c. The absence of any phase contrast suggests that the carbon-induced structures are located underneath (instead of on top of) the outermost MoS_2 layer(s). In order to confirm this observation, we have performed high-resolution lateral force microscopy (LFM) on top of such a layer, we indeed measure the expected lattice periodicity of MoS_2, see Fig. 1f. Supporting evidence was obtained by STS measurements. Current-Voltage Spectroscopy reveals that both the top of the layers and their surroundings display the same behavior, which corresponds to the bare MoS_2 electronic structure, see Fig. 2. These findings clearly demonstrate that the carbon-induced layers are indeed located in between MoS_2 sheets.

The carbon-induced layers are usually found in close vicinity to MoS_2 steps or defects, indicating that the intercalation of carbon takes place through these pores. An example is shown in Fig. 3a and b, where carbon-induced layers were formed inward from a MoS_2 step and through a one-dimensional defect, respectively. These results clearly demonstrate the formation of carbon-induced layers between MoS_2 tri-layers. The MoS_2 surface is impermeable to small molecules such as ethylene and it is thus impossible for the ethylene molecules to penetrate through a perfect top MoS_2 tri-layer. Intercalation can occur between any of the MoS_2 sheets as long as there is a defect that allows intercalation of