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Full Length Article

Layer-by-layer thinning of $MoSe_2$ by soft and reactive plasma etching

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ABSTRACT

Two-dimensional (2D) transition metal dichalcogenides (TMDs) like molybdenum diselenide ($MoSe_2$) have recently gained considerable interest since their properties are complementary to those of graphene. Unlike gapless graphene, the band structure of $MoSe_2$ can be changed from the indirect band gap to the direct band gap when $MoSe_2$ changed from bulk material to monolayer. This transition from multilayer to monolayer requires atomic-layer-precision thining of thick $MoSe_2$ layers without damaging the remaining layers. Here, we present atomic-layer-precision thinning of $MoSe_2$ nanaosheets down to monolayer by using $SF_6 + N_2$ plasmas, which has been demonstrated to be soft, selective and high-throughput. Optical microscopy, atomic force microscopy, Raman and photoluminescence spectra suggest that equal numbers of $MoSe_2$ layers can be removed uniformly regardless of their initial thickness, without affecting the underlying SiO_2 substrate and the remaining $MoSe_2$ layers. By adjusting the etching rates we can achieve complete $MoSe_2$ removal and any disired number of $MoSe_2$ layers including monolayer. This soft plasma etching method is highly reliable and compatible with the semiconductor manufacturing processes, thereby holding great promise for various 2D materials and TMD-based devices.

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1. Introduction

A new type of two-dimensional (2D) layer-structured nano materials, represented by graphene and transition metal dichalcogenides (TMDs), has aroused a worldwide research fever since 2004 [1–5]. These 2D materials can be exfoliated from their 3D bulk counterparts because of the weak van der Walls force between the layers [6,7]. Nevertheless, unlike conductive graphene with gapless characteristic, TMDs, such as $MoSe_2$, MoS_2 and WS_2, are semiconducting materials, and different energy band gap have been observed for different numbers of TMD layers [8,9]. Molybdenum diselenide ($MoSe_2$), a member of the TMDs family, has many excellent physical, chemical and mechanical properties. For instance, when $MoSe_2$ changed from bulk material to monolayer, the band structure can be changed from the indirect band gap ($Eg = 1.1$ eV) to the direct band gap ($Eg = 1.55$ eV) [10,14]. Therefore, the photoluminescence intensity increases gradually as the number of $MoSe_2$ layers decreases from multiple layers to few-layer and monolayer and it is advantageous to prepare thin film light-emitting devices using few-layer $MoSe_2$ [10–13]. Due to its excellent catalytic activity, $MoSe_2$ can also be used as the cathode material of photoelectrochemical cell for hydrogen production with high stability even if the photoelectrochemical cell is circled for one thousand times [15]. In addition, $MoSe_2$ monolayer can absorb 5–10% of the incident visible light and this absorbency is one order of magnitude higher than that of Si and GaAs with the same thickness [16].

Therefore, the thickness tailoring and engineering of thin-layer $MoSe_2$ are of great importance for the preparation of various $MoSe_2$-based devices. Chemical vapor deposition (CVD) is the most common method to synthesize large area $MoSe_2$ monolayers [17], but the process temperature is often too high and the reproducibility is poor. Both mechanical [10] and liquid exfoliation [18] methods have been used to successfully obtain high quality few-layer and monolayer TMD materials, including $MoSe_2$. However, exfoliated TMD films usually contain non-uniform domains with different number of layers and thus the production efficiency of such methods is low [19]. Post-growth thinning by methods of thermal annealing, laser and plasma etching has been actively pursued for achieving high-quality few-layer or monolayer TMD materials [19–23]. In particular, we demonstrated a versatile and effective plasma technique for the soft, selective and uniform layer-by-layer etching of MoS_2 using $SF_6 + N_2$ precursors in our previous report [23]. In the work presented here, this soft plasma technique is also shown to be applicable for the thickness tailoring and engineering

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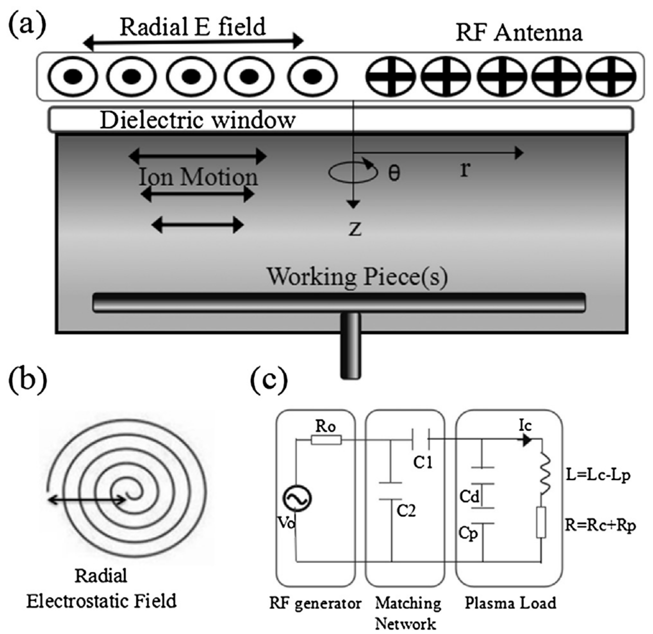

Fig. 1. (a) The schematic diagram of mild plasma deposition system; (b) Plane spiral coil; (c) The energy transport mechanism of the system.

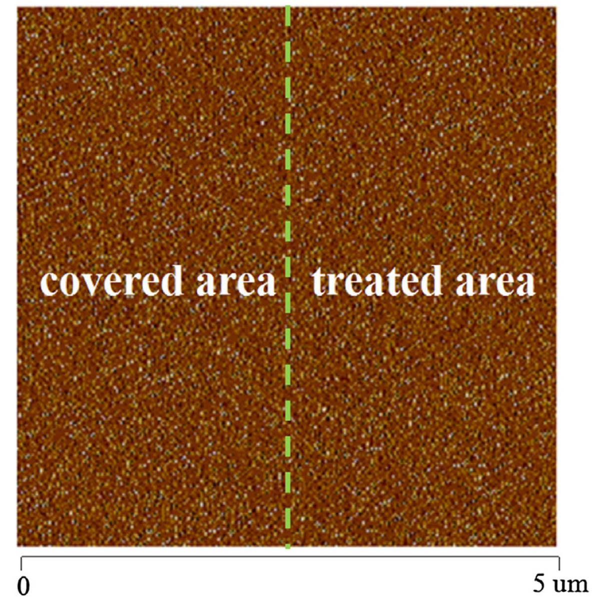

Fig. 2. A representative AFM surface morphology of the SiO_2/Si substrate consisting of the treated area under $SF_6 + N_2$ plasma environment for 2 h and the covered area.

of thin-layer $MoSe_2$. As our previous work reported, this approach is based on reactive plasma where the ion impact is intentionally reduced by generating the majority of the electrons with the energies insufficient for the effective ion generation or causing damage to the remaining layers. The reactive radicals generated in such plasma uniformly remove equal numbers of $MoSe_2$ layers irrespective of the initial thickness, without affecting the underlying SiO_2 substrate and the exposed $MoSe_2$ layers. Optical microscopy (OM), Raman [24,25], photoluminescence [25–27] (PL) and atomic force microscopy [27,28] (AFM) measurements are used to confirm the thickness change in $MoSe_2$ layers.

2. Experimental

The initial thick $MoSe_2$ flakes were mechanically exfoliated from bulk $MoSe_2$ single-crystals onto Si/SiO_2 (300 nm oxide) substrates. The thicknesses of these samples were measured by a combination of optical microscopy, Raman spectroscopy and atomic force microscopy. A single Se-Mo-Se layer is assumed to be 0.9 nm in thickness. A planar low-frequency (0.5 MHz) inductively-coupled plasma (ICP) source was applied to etch the $MoSe_2$ flakes at room temperature. The schematic diagram of the plasma etching system is shown in Fig. 1(a). Although the plasma is generated by an inductive coil antenna, the plasma operates in the capacitive discharge mode (E-mode). As shown in Fig. 1(b), the capacitive coupling originating from the planar spiral coil can produce radial electrostatic field parallel to the substrate surface. Fig. 1(c) shows the energy transport mechanism of the soft plasma system. The energy of RF generator was transferred from planar spiral coil to plasma in both capacitive and inductive modes. The capacitively-coupled electrostatic field is originated from the radial potential drop across the two ends of the planar induction coil while the inductively-coupled electric field was induced by the mutual induction between the coil and plasma. At low input RF power (in E mode), the induced electric field is much smaller than the radial electrostatic field due to low coil current and thicker plasma sheath. At this stage, direct ionization of feedstock gas by radial electrostatic field takes place but most of the generated electrons do not gain sufficient kinetic energy to initiate further ionization collisions. This leads to low ionization rate and low electron density (of the order of magnitude of 10^9–10^{10} cm^{-3}) in this regime. As such, the ion density was too low to induce destructive ion bombardment onto the processed samples [23,29] and this is how the soft plasma etching works.

The plasma was excited in the capacitive discharge mode (E-mode) with the precursor gases of N_2 (at the flow rate of 1.0 sccm) and SF_6 (at the flow rate of 4.5 sccm) at a working pressure of 3.8 Pa. Whether the plasma etching is soft or harsh depended strongly on the input power density, with a critical value of ~1.5 mW/cm^3. Therefore, we adopted two low input power densities at 0.8 and 1.2 mW/cm^3 for the fine and fast etching modes, respectively. The optical images are obtained by a Leica 4200 Optical Microscopy. The Raman and photoluminescence spectra are recorded using a LabRAM HR Evolution Raman system with 532 nm laser excitation. The laser power at the sample is lower than 0.5 mW, so as to avoid the laser-induced heating damage. AFM is carried out by a bruker dimension ICON system.

3. Results and discussion

The etching mechanism in this work is quite similar to what we have demonstrated for MoS_2 etching in our previous report [23]. In contrast to the traditional plasma etching environment where high-energy ions produced by high-density plasma are used as the main etching source, the present soft etching process utilizes radical reaction instead of ion bombardment via a plasma chemistry based on the $SF_6 + N_2$ precursors. The reactions and chemicals induced in the soft plasma etching process using $SF_6 + N_2$ precursors are given as follow:

$$3SF_6 + N_2 \rightarrow 2NF_3 + 3SF_4 \quad (1)$$

$$3MoSe_2 + 16NF_3 \rightarrow 8N_2 + 3MoF_4 + 6SeF_6 \quad (2)$$

$$2MoF_4 \rightarrow 2MoF_3 + F_2 \quad (3)$$

Compared to the case of MoS_2 etching with all volatile by-products including MoF_4 [23], MoF_3, F_2, SF_4 and SF_6, there is only one different by-product namely SeF_6 in the present case. The volatile property of SeF_6 confirms the applicability of this soft etching technique for $MoSe_2$ as well. The plasma chemistry offers several advantageous features: (i) the by-product NF_3 generated

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