Synthesis of large scale MoS_2 for electronics and energy applications

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Layered molybdenum disulfide (MoS_2) has attracted great attention owing to its unique properties. However, synthesizing large area thin film with high crystal quality and uniformity remains a challenge. The present study explores large scale MoS_2 growth methods, i.e., two-step method of sputtering-chemical vapor deposition and direct sputtering method, and applies them to fabricate field effect transistors and supercapacitors, respectively. The thickness modulated MoS_2 films by two-step method exhibited high field effect mobility [$\sim$12.24 $cm^2/(V\ s)$] and current on/off ratio ($\sim 10^6$). The direct sputtering of MoS_2 demonstrated excellent electrochemical performance with a high capacitance ($\sim$30 mF/cm^2) and cyclic stability upto 5000 cycles. Our growth methods reported here for the large scale MoS_2 with high uniformity can trigger the development of several important technologies in two-dimensional materials.

I. INTRODUCTION

The demand in the high efficiency electronics and energy storage devices has compelled researchers to explore novel two-dimensional (2D) transition metal dichalcogenide materials and their fabrication techniques.[1,2] Recently, 2D molybdenum disulfide (MoS_2) has been intensively studied as semiconducting material analogous to graphene.[3–5] Unlike graphene, MoS_2 is an indirect band gap (1.2 eV) semiconductor that changes to a direct band gap (1.8 eV) when it is scaled down a single layer (SL), making it suitable for field effect transistors (FETs), photodiodes and other optoelectronic devices.[6–9] Besides this, the efficient electrochemical intercalation of electrolyte ions (H^+, Li^+, K^+) into MoS_2 nanosheets together with the high surface area of 2D structure renders its use in electrochemical energy storage devices such as batteries and supercapacitors.[10]

There has been significant research on the production of 2D MoS_2 using mechanical and chemical exfoliation methods.[11–13] While these methods are useful to produce high quality MoS_2 flakes, they have a poor yield and are not suitable for scalable device applications where uniform and large scale deposition is desired. Another method commonly used to grow thin film MoS_2 is the vapor-phase reaction of MoO_3 and S powders in a chemical vapor deposition (CVD) system.[14] Although this technique has shown continuous film of MoS_2, it often results in the formation of randomly distributed flakes rather than a continuous film. Hence, there is a big demand to grow thickness-controlled, large scale, and uniform MoS_2 films.

Herein, we present large scale growth of MoS_2 films; two-step method of sputtering-CVD and direct sputter deposition of MoS_2 films, and their applications in FET and supercapacitor, respectively. The sputtering technique involved in our growth methods offers substantial control over the deposition rate which enables the engineering of MoS_2 thickness on various substrates including flexible and transparent polymer-based substrates.[15] The MoS_2 FET exhibited superior mobility and high on/off ratio, and the MoS_2-supercapacitor electrode demonstrated a very high capacity and cyclic stability as compared to previously reported results on MoS_2-based electrodes.

II. MoS_2 FOR ELECTRONICS APPLICATIONS

A. MoS_2 film growth by two-step method

MoS_2 growth in our lab using the two-step method [Fig. 1(a)] involves the room temperature deposition of parent Mo films on Si/SiO_2 substrates as the first step. Mo films with different thicknesses were prepared by controlling the sputter deposition time. A high-purity (99.99%) Mo metal target of 50 mm in diameter was used for sputtering Mo thin films. The substrates were initially cleaned thoroughly with acetone in an ultrasonic bath, followed by cleaning in ethanol, methanol, and

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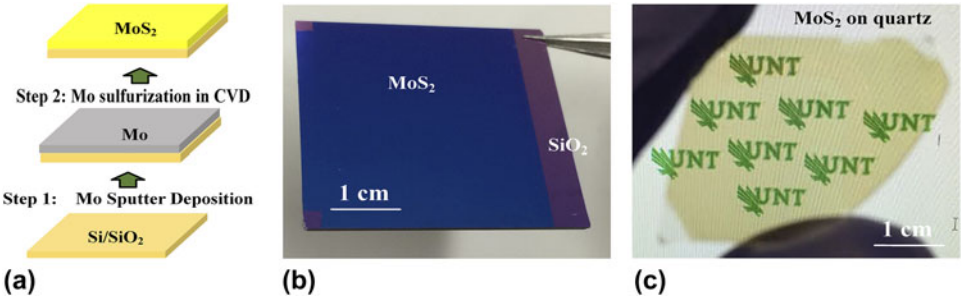


FIG. 1. (a) Schematic showing the two-step growth method; Step 1: Deposition of Mo film using magnetron sputtering, Step 2: Sulfurization of Mo films in a CVD furnace. Large area growth of MoS_2 on (b) Si/SiO_2 and (c) transparent (quartz) substrate.

deionized (DI) water. The substrates were fixed on the heater, and the chamber was evacuated to a vacuum level of 10^{-7} Torr. Before every sputtering run, the target was presputtered for 5 min to ascertain the same state of Mo target for each sample. In the second step, the deposited Mo films were subsequently placed in a low-pressure CVD system (graphene square CVD) equipped with a 4 inch diameter quartz tube furnace. A ceramic boat containing pure sulfur (~1 gm, Sigma Aldrich, St. Louis, Missouri) was placed in the upstream of the quartz tube. Argon was used as a carrier gas to convey sulfur vapor species to the Mo films. The tube was pumped down to a pressure of 10^{-3} Torr and flushed with Ar gas repeatedly to guarantee a favorable growth atmosphere. In the flow atmosphere of 200 sccm Ar with a chamber pressure of 5 Torr, the furnace was heated to 600 °C at the center zone in 30 min. After 60 min, the furnace was cooled down naturally to room temperature. Figures 1(b) and 1(c) show the optical images of large area MoS_2 film grown on Si/SiO_2 and quartz substrates, respectively. These films can be further transferred to any arbitrary substrates using KOH solution and DI water. The sample names S_1, S_2, S_3, S_4, and S_5 are used for Mo films deposited for 4, 10, 30, 60, and 180 s, respectively.

B. Characterization of grown MoS_2 film

MoS_2 films synthesized by using the two-step method were characterized to confirm their thickness, crystalline quality, and uniformity over the wafer scale. Figures 2(a) and 2(b) show the atomic force microscopy (AFM) image and corresponding height profile of MoS_2 film for sample S_1. A step height of 0.728 nm infers the presence of SL MoS_2. To further confirm the thickness, cross-sectional high resolution transmission electron microscopy (HRTEM) image was recorded as shown in Fig. 2(c). However, the HRTEM image represents a SL MoS_2 thickness, but the film was not uniform over the entire region of the cross-section. The formation of voids or breakage as seen in the image could be attributed to very low sputter deposition time and polycrystalline nature of the MoS_2 film. Raman spectroscopy is an excellent tool to address the evolution of structural properties in layered materials changing their thickness from the 3D bulk to 2D van der Waal layered structures.[16] The Raman spectrum of bulk MoS_2 has two vibration modes: an in-plane (E_{2g}) mode located around 383 cm^{-1} and an out-of-plane (A_{1g}) mode, which is located at 407 cm^{-1}. The difference of frequencies between these two modes could be used to identify the number of layers in MoS_2 films. Figure 2(d) shows the Raman spectra of MoS_2 films with different thicknesses, measured at 532 nm excitation laser line. A frequency difference (Δk) of ~19.7 cm^{-1} observed in sample S_1 confirms a SL MoS_2,[17] whereas this frequency difference rises with increasing number of layers, indicating the modulation of MoS_2 film thickness. The thickness of the MoS_2 film corresponding to sample S_2, S_3, S_4, and S_5 as estimated by AFM height profile measurements was found to be 3.38, 5.48, 7.11, and 12.20 nm, respectively [Fig. 2(e)]. We also developed a simple and nondestructive method to identify the number of MoS_2 layers by using the optical contrast of thickness modulated MoS_2 films. The detail study of this method is published elsewhere.[18] Figure 2(f) shows the optical images of MoS_2 films grown on Si/SiO_2 substrate taken by Nikon Eclipse ME600 microscope (Melville, New York). It is to be noted that the color of MoS_2 film changes from purple to green with increasing number of MoS_2 layers. The change in MoS_2 color could be due to the change in optical band gap energy and reflectance with changing thickness.[19] The facile optical contrast and color methods of thickness identification could be applied to a variety of substrate systems. The detail method for identifying MoS_2 thickness on different substrate systems is under investigation.

C. Field effect transistors

One of the most important application for semiconducting MoS_2 is in FETs for next generation electronic devices.[20] There have been several efforts in fabricating MoS_2 FETs using mechanical exfoliation and CVD methods but the mobility on SiO_2 substrates is typically characterized at low value of 0.01–10 $cm^2/(V\ s)$.[21,22]

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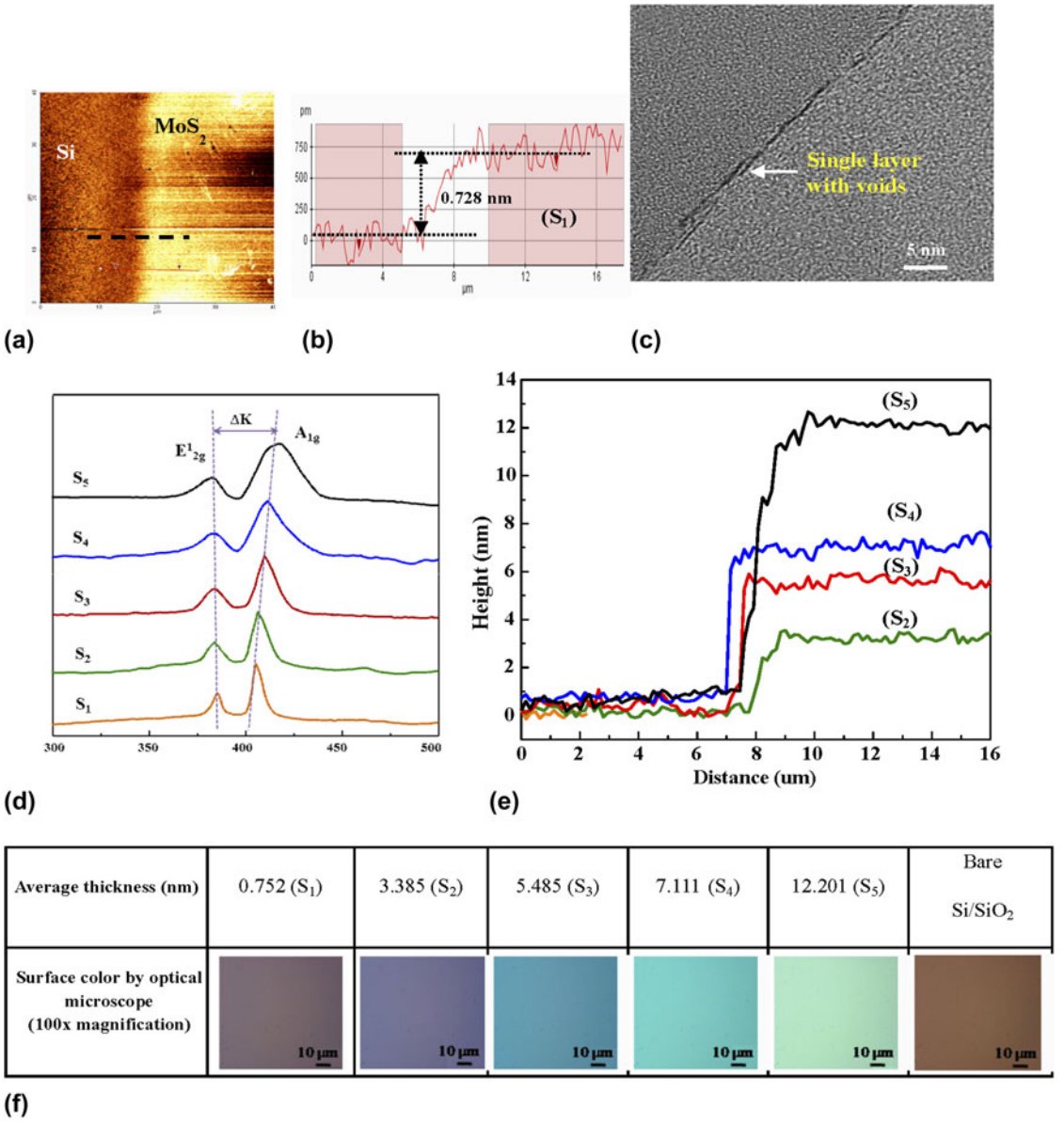


FIG. 2. MoS_2 characterization fabricated by two-step method (a) AFM image and (b) height profile of MoS_2 film on SiO_2 substrate (sample S_1), (c) cross-section HRTEM image of S_1 showing voids and discontinuous film, (d) Raman spectra of MoS_2 film with different thicknesses. Peaks shifts apart with increasing thickness, (e) AFM height profiles of MoS_2 films with different thicknesses (S_2–S_5), and (f) optical images showing the color variation in MoS_2 films with increasing thickness from sample S_1 to S_5.

Radisavljevic et al.[6] used HfO_2 gate dielectric for SL MoS_2 transistor and reported an outstanding mobility of 200 $cm^2/(V\ s)$ and current on/off ratio of 1×10^8 at room temperature. However, the fabrication of MoS_2 FET devices by using above methods resulted in non-uniform small flakes without any control over the film thickness. Therefore, it is imperative to develop new fabrication methods for scalable and layered controlled synthesis of MoS_2 films for commercial electronics applications.

The wafer scale and thickness modulated MoS_2 films fabricated by using our two-step method were characterized for electrical performance. Figure 3(a) shows the variation of electrical resistance with increasing MoS_2 film thickness, measured at room temperature. It could be observed from the graph that sample S_1 shows very high resistances while the resistance decreases with increasing MoS_2 thickness (S_2 & S_3) and shows a metallic conductance for thicker MoS_2 films (S_4 & S_5). The very high resistance in sample S_1 could be attributed to the discontinuity or void formation and large spatial constraints imposed by the underlying substrate. The electrical measurement for this sample did not show any FET behavior. However, a good FET behavior with p-type

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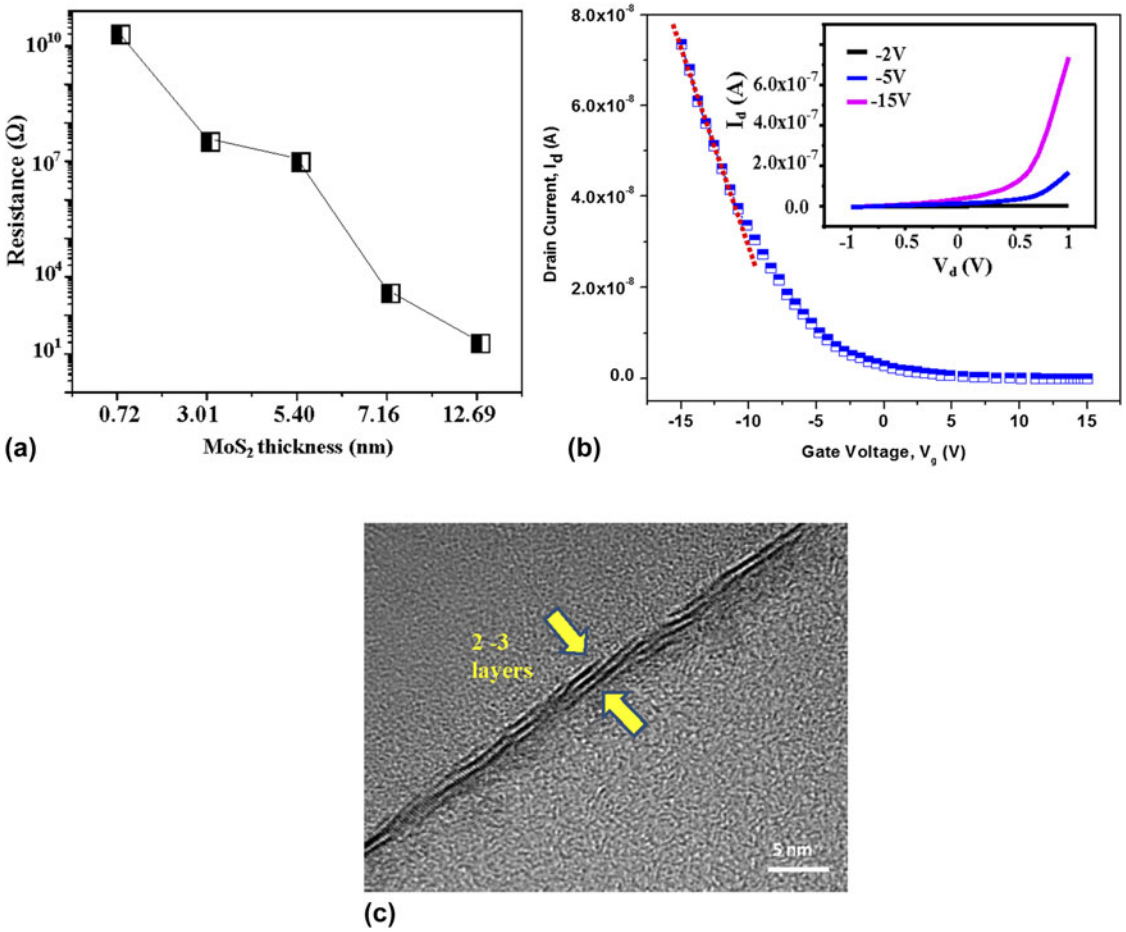


FIG. 3. (a) Electrical resistance of MoS_2 film with varying thickness, (b) FET properties shown by sample S_2, and (c) HRTEM cross-section of 2–3 layers MoS_2, indicating a complete sulfurization and uniform MoS_2 growth.

conduction was observed in sample S_2 as shown in Fig. 3(b). The mobility and current $I_{on/off}$ recorded for sample S_2 were ~12.24 $cm^2/(V\ s)$ and ~1.56 × 10^6, respectively.[23] Our results are better than many previous reports on mechanically exfoliated and CVD grown MoS_2 atomic layers. Generally, most of the MoS_2-based FETs showed n-type behavior but the origin of the electron doping is still unclear and need more investigation. On the other hand, there are only few studies showing a p-type conduction in MoS_2.[24] We believe that the p-type behavior might have originated from the localized trap states that are expected to be present at the interface of the Si/SiO_2 substrate and MoS_2 film, which tends to relocate the Fermi level of the SiO_2/MoS_2 system just below the valence band maxima, making the system a p-type semiconductor. For higher MoS_2 thickness (12.29 nm), a conducting electrical behavior with a high value of drain current was observed in the FET measurements. It could be attributed to the presence of unsulfurized Mo films at MoS_2-substrate interface. Hence, there is a critical thickness limit upto which Mo can be fully sulfurized by using the same set of experimental conditions. Figure 3(c) shows the cross-section image of MoS_2 film from sample S_2 demonstrating high uniformity and complete sulfurization of the Mo film.

III. MoS_2 FOR ENERGY APPLICATIONS

A. MoS_2 film growth by direct deposition

2D MoS_2 also has been attracted as a promising supercapacitor electrode material due to its intriguing sheet-like structure that provides large surface area for double layer charge storage and the presence of multiple oxidation states in the Mo atom facilitating pseudocapacitance by the intercalation of electrolyte ions (H^+; Li^+) into S–Mo–S nanosheets. However, relatively thick films are needed for the sufficient charge storage and for the reliable performance of the material.[25] We found that the direct deposition of MoS_2 by sputtering is an efficient method to make a desired structure of MoS_2 for a large scale supercapacitor electrode on any substrate including flexible substrates. Hence, we fabricated a flexible MoS_2 thin film electrode and characterized its performance in supercapacitor. It is also noted that this method offers the

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possibility of MoS_2 deposition on complex surfaces with high uniformity on larger cross-section and better adhesion as compared to previously reported results on chemically exfoliated or CVD grown films. In addition, these methods are accompanied with residues and contaminants. Figure 4(a) shows the schematic of MoS_2 deposition directly on various substrates including Cu foil, Si/SiO_2, and polyimide. The MoS_2 films were deposited at low substrate temperature of 300 °C by direct sputtering of MoS_2 target (99.8% purity) at a radio frequency (RF)

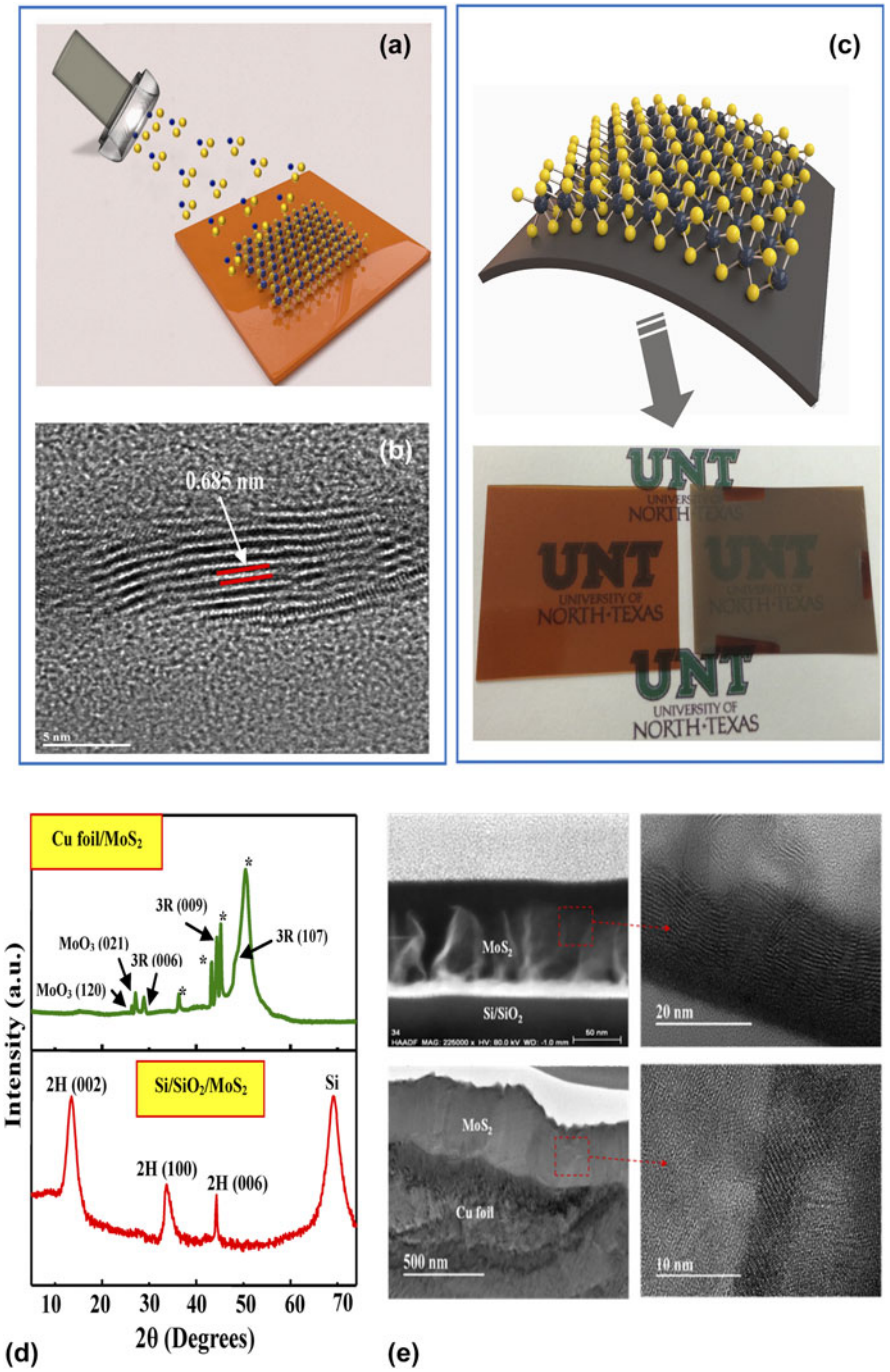


FIG. 4. (a) Schematic diagram showing the direct sputter deposition of MoS_2 films, (b) HRTEM image clearly shows the formation of high quality MoS_2 film by sputtering method, (c) schematic diagram showing the potential of direct deposition on flexible substrates. Camera images demonstrating MoS_2 film grown on polyimide substrate in our lab, (d) XRD patterns revealing 2H and 3R MoS_2 structure in MoS_2 films deposited on Si/SiO_2 substrate and Cu foil, respectively (peaks shown by asterisk are from Cu substrate), and (e) cross-sectional HRTEM and morphology of MoS_2 film on Si/SiO_2 and Cu substrates.

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power of 60 W in an inert gas plasma (Argon ~99.999% purity).

B. Characterization of direct deposited MoS_2 films

Although, there are several studies in the past that utilized sputtering to deposit MoS_2 coatings for solid lubricant applications,[26] the reports on the fabrication of MoS_2 films for electronics and energy applications by direct sputtering are sparse. Voevodin and co-workers[27] attempted to grow 3–6 molecular layers of MoS_2 on thermally grown silicon oxide and (002) graphite using magnetron sputtering at a growth temperature of only 350 °C. In another study, Alam et al.[28] studied the dependence of grain size on temperature by in situ heating of free standing MoS_2 in transmission electron microscopy. In this context, our research group succeeded in fabricating high quality, large scale MoS_2 films on different substrates by using direct sputtering technique. The HRTEM image of Fig. 4(b) demonstrates the formation of high quality MoS_2 films on Cu foil. The thickness of individual layer was found to be 0.685 nm, which is the typical thickness of SL MoS_2.[29] The possibility of low temperature deposition (~300 °C) enabled us to grow MoS_2 layers on other flexible substrates like polyimide [Fig. 4(c)]. Interestingly, we found that MoS_2 films deposited on different substrates exhibited different crystal structures. It is clear from the X-ray diffraction (XRD) spectra of Fig. 4(d) that MoS_2 films grown on Si/SiO_2 substrates exhibited a hexagonal (2H) phase while a rhombohedral (3R) phase was indexed by the XRD results when MoS_2 was deposited on Cu foil. The formation of different crystalline structures in our MoS_2 films could be attributed to the fact that the crystalline structure of sputtered deposited MoS_2 films depends on the chemically active sites, surface smoothness, and roughness of the substrates.[30] In our case, SiO_2 surface is much smoother as

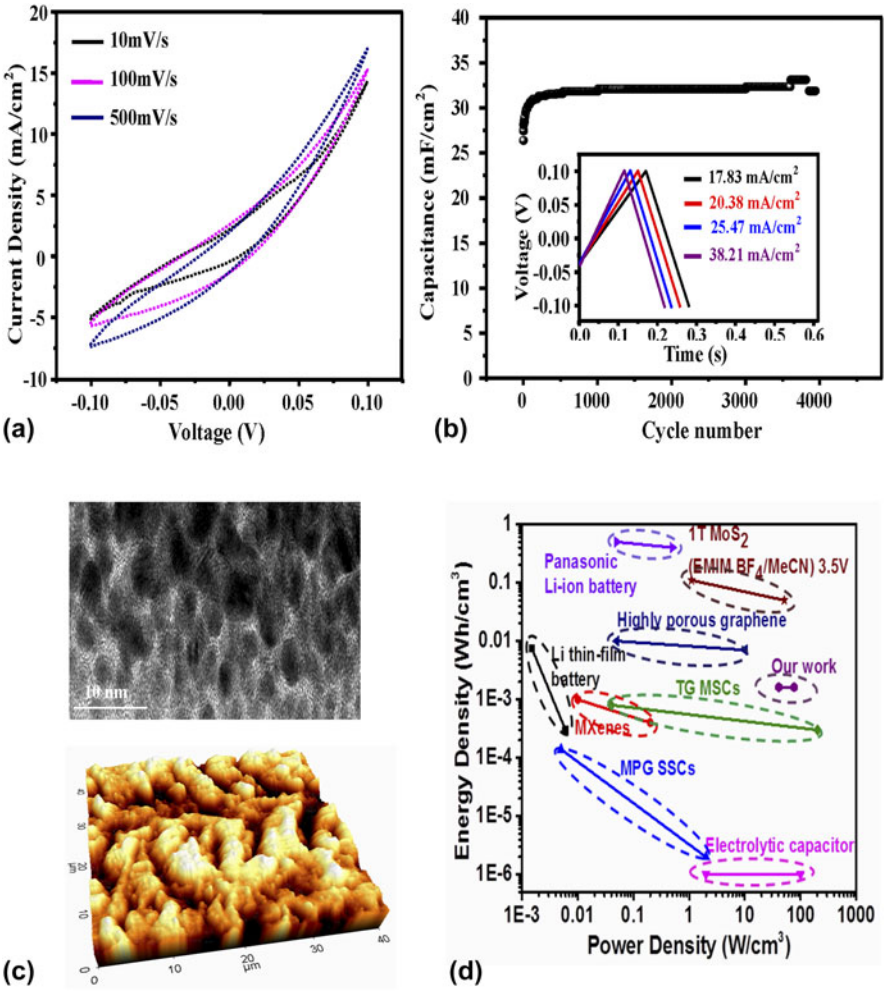


FIG. 5. (a) CV curves at different scan rates in 0.5 M H_2SO_4 electrolyte, (b) capacitance variation with cycle number a current density of 25.47 mA/cm^2. The inset shows the charge–discharge profiles at different current densities, (c) AFM and HRTEM image showing the formation of unique 3D porous MoS_2 structure, and (d) Ragone plot showing comparing the energy and power density of our supercapacitor electrode with different supercapacitor electrodes.

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compared to the Cu foil and therefore possess high chances of layered structure growth (2H) parallel to the substrates. On the other hand, the uneven morphology in Cu foil with large surface roughness may promote the growth of nano-clustered MoS_2 films in highly un-equilibrium conditions and leads to a less stable (3R) polytype. Figure 4(e) shows the HRTEM cross-section and morphology of MoS_2 film on Si/SiO_2 and Cu substrates, respectively. It is observed that MoS_2 film crystallized into a well layered (2H) structure on Si/SiO_2 while a random distribution of MoS_2 layers with a un-equilibrium structure is formed on Cu foil, which is consistent with the XRD results.

C. MoS_2 for supercapacitors

The MoS_2 films deposited on Cu foil were used as supercapacitor electrode and its electrochemical performance was evaluated by using cyclic voltammetry (CV). Charge storage in MoS_2 thin films can be done by three ways: (a) double layer charge storage by individual interlayer of MoS_2, (b) intra S–Mo–S double layer charge storage due to diffusion of electroactive species into the basal plane, and (c) Faradic charge transfer due to several oxidation states of Mo atoms ranging from +2 to +6 exhibiting pseudocapacitance due to efficient intercalation of alkali ions (H^+, Li^+, Na^+, and K^+).[31,32]

Figure 5(a) shows the CV results of our MoS_2 electrode at different scan rates ranging from 10 mV/s to 500 mV/s. The elliptical *S*-shape curve of the CV indicates the combination of double layer charge storage and pseudocapacitance mechanism in our electrode.[28] The observed deviation from the ideal rectangular characteristics is mainly attributed to large polarization of electrode and physical/chemical adsorption at the interface. Furthermore, galvanostatic charge/discharge tests were performed at a current density of 25.47 mA/cm^2. An excellent electrochemical performance with a capacitance of ~30 mF/cm^2 and cyclic stability up to 4000 cycles could be observed in Fig. 5(b). The existence of linear and triangular charge/discharge profile at different current densities [inset of Fig. 5(b)] represents the dominance of double layer charge storage mechanism. A small equivalent series resistance of only ~3 Ω was also calculated from the Nyquist plot of our electrodes (not shown here). The excellent electrochemical performance observed in our MoS_2 electrodes could be attributed to the open porous structure with a 3D MoS_2 island structure shown by the HRTEM and AFM image of the top surface of the MoS_2 film [Fig. 5(c)]. This unique structure facilitates ample open channels for the large ion transport and penetration of electrolytic ions into the pores leads to high capacitive performance. Figure 5(d) compares the volumetric power and energy densities of our MoS_2 electrode with other commonly used power sources. It is observed that the power density of our supercapacitor electrode (~80 W/cm^3) surpasses the previously reported values and the volumetric energy density (1.62–2.33 mWh/cm^3) exceeds conventional activated carbon and electrolytic capacitors. The interesting electrochemical properties of MoS_2 film makes it attractive as a promising electrode for the next generation supercapacitor energy storage devices.

IV. CONCLUSIONS

The present studies explore the growth of large scale MoS_2 thin films for potential applications in electronics and energy storage devices. The two-step sputtering-CVD and direct deposition by magnetron sputtering methods were developed to grow large scale, uniform, and thickness modulated MoS_2 films. Raman, AFM, and HRTEM techniques were used to confirm the uniformity and atomic layered structure of MoS_2 films. FET measurements on our MoS_2 films grown by two-step method exhibited a high field effect mobility and current on/off ratio. High performance supercapacitor electrodes exhibiting high capacitance (~30 mF/cm^2) and long cyclic stability were fabricated using the direct deposition of MoS_2 films on Cu foils. Direct deposition by sputtering offers an advantage for wafer scale MoS_2 films growth directly on flexible substrate. The current approaches of large scale MoS_2 deposition with interesting results will definitely trigger important technological advancement taking MoS_2 film from the laboratory to industrial applications.

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