Applied Surface Science 297 (2014) 139–146

Contents lists available at ScienceDirect

Applied Surface Science

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

Controlled synthesis of transition metal dichalcogenide thin films for electronic applications

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ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 15 January 2014
Accepted 16 January 2014
Available online 27 January 2014

Keywords:
2D materials
Transition metal dichalcogenides
Nanoelectronics
Sensors
Spectroscopy
Thin films

ABSTRACT

Two dimensional transition metal dichalcogenides (TMDs) are exciting materials for future applications in nanoelectronics, nanophotonics and sensing. In particular, sulfides and selenides of molybdenum (Mo) and tungsten (W) have attracted interest as they possess a band gap, which is important for integration into electronic device structures. However, the low throughput synthesis of high quality TMD thin films has thus far hindered the development of devices, and so a scalable method is required to fully exploit their exceptional properties. Within this work a facile route to the manufacture of devices from MoS_2 and WS_2, grown by vapour phase sulfurisation of pre-deposited metal layers, is presented. Highly homogenous TMD films are produced over large areas. Fine control over TMD film thickness, down to a few layers, is achieved by modifying the thickness of the pre-deposited metal layer. The films are characterised by Raman spectroscopy, electron microscopy and X-ray photoelectron spectroscopy. The thinnest films exhibit photoluminescence, as predicted for monolayer MoS_2 films, due to confinement in two dimensions. By using shadow mask lithography, films with well-defined geometries were produced and subsequently integrated with standard microprocessing process flows and electrically characterised. In this way, MoS_2 based sensors were produced, displaying sensitivity to NH_3 down to 400 ppb. Our device manufacture is versatile, and is adaptable for future nanoscale (opto-) electronic devices as it is reproducible, cost effective and scalable up to wafer scale.

1. Introduction

The novel properties of two dimensional semiconducting transition metal dichalcogenides (TMDs) make them of great interest for both academia and industry [1–3]. They offer an exciting alternative to graphene, as they possess a band gap, which is crucial for applications in electronics and photonics. These materials have the general formula MX_2 with M being a transition metal (commonly, but not limited to, Mo, W, Nb, Ta, Ti); and X being a chalcogen (S, Se, Te). This class can form two-dimensional layered films composed of a plane of metal atoms covalently bonded to chalcogen atoms. Bulk crystals of such materials have long been studied[4], but in recent years the isolation of their 2D analogues has led to renewed interest in this field.

Importantly, a transition from an indirect gap to a direct gap semiconductor has been reported for MoS_2 [5], and WS_2 [6,7] as they approach monolayer thickness. Single layer MoS_2 shows a transition from the bulk indirect band gap of 1.2 eV, to a direct band gap of 1.9 eV [8]. The WS_2 analogue shows a similar transition with a bulk indirect band gap and monolayer direct band gap of 1.4 eV and 1.8 eV, respectively [9]. Recent work has used micromechanically exfoliated layers to produce devices which demonstrate excellent on/off ratios and rapid switching [10–12]. Layers exfoliated by this method have been shown to display photoluminescence (PL) [13] and electroluminescence [14], and thus have potential applicability in optoelectronic devices. However, this production method is very laborious and offers no prospect of scalability.

Scalable production of 2D TMDs has recently been achieved using sonication assisted liquid phase exfoliation in organic solvents [15] and surfactant media [16] as well as by Li intercalation [17,18] and by thermal decomposition of tetrathiomolybdates (or tetrathiotungstates) [19]. Such methods can be used to produce bulk quantities, well suited for applications in composites [20–23], catalysis [19], lithium ion batteries [24,25] and supercapacitors

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http://dx.doi.org/10.1016/j.apsusc.2014.01.103

[26]. However, they are not readily compatible with standard microprocessing techniques; and the films produced from individual flakes display inferior electronic properties to those obtained by mechanical exfoliation [27]. Chemical vapour deposition (CVD) is a versatile, cost effective and industry compatible technique, which has greatly advanced graphene research in recent years by making high quality films readily available [28,29]. Similar methods can be used for the production of TMD films, and several routes to the production of MoS_2 thin films have recently been outlined. These typically are not pure CVD processes but rather involve thermally assisted sulfurisation of Mo [30–32] or, more commonly, MoO_3 [33–36], however the use of liquid phase precursors has also been demonstrated [37,38]. WS_2 has similarly been produced through the thermally assisted sulfurisation of WO_3 [33] and W [39] or by atomic layer deposition [40]. However, fine control of TMD layer thickness over large areas, in combination with structured growth, has seldom been demonstrated.

Within this work a facile route to manufacture of devices from TMDs, grown by vapour phase sulfurisation, is presented. Highly homogenous TMD films are produced over large areas by sulfurisation of pre-deposited metal layers. This is demonstrated for MoS_2 and WS_2, but can potentially be extended to produce other TMDs. The thickness of the samples is well controlled, from bulk down to monolayer, and high quality homogenous films are produced over a centimetre scale. The uniformity of these films, as observed through scanning Raman analysis, signifies an advance on existing reports on the sulfurisation of Mo which typically show non-uniform films with limited thickness control [31]. By using shadow masks we obtain films with well-defined geometries that can be readily integrated with standard micro-processing technologies. This procedure minimises processing steps, and results in quick, cost effective and versatile device manufacture.

One area of application, which is highly technologically relevant, is chemical sensors. The ever increasing demand for highly sensitive, low cost and low power sensors, in particular for standalone and mobile systems, has necessitated the investigation of new materials. Electronic gas sensors, based on 1D and 2D nanomaterials in a field effect transistor (FET) configuration, have shown considerable promise [41–43]. Improvements in their sensitivity and selectivity have continuously been demonstrated through covalent or non-covalent functionalisation [44–46]. As a semiconducting analogue of graphene, which has demonstrated single molecule detection [43], 2D MoS_2 is an exciting candidate for future sensors. A number of MoS_2 based gas sensors have recently been reported using micromechanically exfoliated [11,47,48] and liquid phase exfoliated [49,50] MoS_2 flakes. However, these approaches suffer from the previously mentioned problems of poor scalability and poor electronic quality, respectively and it is only recently that devices from more scalable processes have been reported [51]. In this study, we show that our simple process flow is capable of producing gas sensing devices with ultra-high sensitivities, down to 400 ppb for ammonia.

2. Experimental

Thin metal films (Mo, W, 99.99% MaTecK) were sputtered onto substrates (300 nm SiO_2 on Si and fused quartz, Alfa Aesar) using a Gatan Precision Etching Coating System (PECS) allowing for variable thicknesses (0.5–20 nm). The film deposition rate, and thickness, was monitored using a quartz crystal microbalance, maintaining a deposition rate of <0.1 nm/s. Hard masks were used to pattern the coatings, thus defining selective areas of film growth.

Substrates were placed in a quartz tube furnace (Lindberg Blue) and heated (~50 °C/min) to 500 °C under Ar flow (150 sccm, $P \sim 0.7$ Torr). After a 5 min dwell at 500 °C, the samples were heated to 750 °C (25 °C/min) and annealed for 30 min. A second upstream hot zone was used to melt S powder (MaTecK, 99%) to 113 ± 0.1 °C, and thus introduce S vapour into the reaction zone. This hot zone consisted of an assembly of halogen bulbs coupled with a power supply. A k-type thermocouple, placed alongside the S supply, allowed for the temperature in the vicinity of the S powder to be monitored. Following sulfurisation, the samples were held at 750 °C for a further 20 min, before the furnace was cooled. Upon removal from the furnace, samples were cleaned with acetone and then isopropanol (both HPLC grade) to remove unreacted residue.

For deposition of metal leads a hard mask was aligned to the pre-structured TMD films and Ti/Au (10/80 nm) was deposited with the Gatan PECS.

High resolution transmission electron microscopy (HRTEM) bright field images were obtained using a FEI Titan 80–300 TEM. Samples were prepared by first spin coating a PMMA support layer onto the MoS_2 thin films and then etching the substrate with 15 M KOH. Samples were then transferred to lacey carbon TEM grids and the PMMA removed by immersion in acetone.

Raman analysis was performed using a Witec Alpha 300R confocal Raman microscope, utilising a 532 nm laser and an 1800 lines/mm grating. A laser power of less than 1 mW was used for all measurements in order to avoid sample damage. Raman maps were obtained by taking 4 scans every μm in the *x* and *y* direction. PL measurements were taken using the same system with a 600 lines/mm grating in a high cm^{-1} regime.

X-ray photoelectron spectroscopy (XPS) was performed under ultra-high vacuum conditions (base pressure of 2×10^{-10} mbar) using a VG Scientific CLAM2 analyser operated at a pass energy of 50 eV with 2 mm slits, giving a FWHM on Ag $3d_{5/2}$ of 1.25 eV for the source (PSP twin anode, unmonochromatised Al K_α, operated at 12 kV and 12 mA). The core-levels were fitted using the software CasaXPS.

Electrical characteristics were measured under ambient conditions using a Karl Suss probe station in conjunction with a Keithley model 2612A source meter.

Gas Sensing measurements were performed in a homemade gas sensing chamber. 200 ppm NH_3 gas, balanced by dry N_2, was introduced into the chamber using mass flow controllers to dilute the gas concentration by mixing with dry N_2. At a 100 sccm flow of the NH_3/N_2 mixture, the gas sensing chamber was kept at a pressure of 10 Torr. The electrical resistance of MoS_2 sensors was measured using a Keithley model 2612A source meter at a constant bias voltage of 0.2 V and all measurements were performed at room temperature. In every test, the MoS_2 sensors were exposed to pure N_2 for 2 min to record their initial resistance and then NH_3 gas was introduced for 2 min, and the sensor response measured. The sensors were exposed to N_2 for 10 min to recover and the gas sensing tests were periodically repeated four times.

3. Results and discussion

TMD thin films were produced by direct sulfurisation of pre-deposited metal films in a quartz tube furnace with two heating zones. MoS_2 formed the primary focus of our study; however our method was also well-suited to the production of WS_2. Thin films of Mo (W) of nominal thicknesses, between 0.5 and 20 nm, were heated to a growth temperature of 750 °C and S powder was then melted in a second upstream heating zone. Using Ar as a carrier gas, S vapour was transported to the substrates, forming MoS_2 (WS_2) at predefined locations. A schematic of this process is shown in Fig. 1a. Films were grown on both SiO_2/Si and fused quartz substrates by sulfurisation of films with different thicknesses of pre-deposited metal. Photographs of MoS_2 films, on both SiO_2/Si