CVD Growth, Defect and Phase Engineering in Two-dimensional Materials for Optoelectronic Applications

A Thesis

Submitted by

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(D14040)

For the award of the degree of

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SCHOOL OF ENGINEERING
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CVD Growth, Defect and Phase Engineering in Two-dimensional Materials for Optoelectronic Applications

Dedicated to

My Parents

&

Sisters

Declaration by the Research Scholar

I hereby declare that the entire work embodied in this thesis entitled "**CVD Growth, Defect and Phase Engineering in Two-dimensional Materials for Optoelectronic Applications**" is the result of investigations carried out by me in the **School of Engineering**, Indian Institute of Technology Mandi, under the supervision of **Dr. Viswanath Balakrishnan** for the award of the degree of **Doctor of Philosophy** is a bona fide record of the research work carried out by me and that it has not been submitted elsewhere for any degree or diploma. In keeping with the general practice, due acknowledgements have been made wherever the work described is based on finding of other investigators.

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Thesis Certificate

I hereby certify that the entire work in this thesis titled "**CVD Growth, Defect and Phase Engineering in Two-dimensional Materials for Optoelectronic Applications**" has been carried out by **Pawan Kumar**, under my supervision in the **School of Engineering,** Indian Institute of Technology Mandi for the award of the degree **Doctor of Philosophy**. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree or diploma.

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PAWAN KUMAR

August, 2018

I am among those who think that science has great beauty. A scientist in his laboratory is not only a technician: he is also a child placed before natural phenomena which impress him like a fairy tale. We should not allow it to be believed that all scientific progress can be reduced to mechanisms, machines, gearings, even though such machinery also has its beauty.

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MARIE CURIE (1867 – 1934)

Preamble

Two-dimensional (2D) materials attracted researchers to explore their fundamental properties as well as industrial applications to great extent. Remarkable properties observed with reduced dimension in these materials made them highly capable in such a way that it can achieve properties that are beyond the current state of technological need. Electrical and optical properties have been explored extensively which giving us a vast field of plausible applications. Chemical vapor deposition (CVD) is known for best growth technique to synthesize the 2D materials with the benefit of high throughput as well as industry scale deliverable capability. Yet several challenges limit further development and needs to be for their advanced product level applications.

In this thesis, firstly (***Chapter 1***) the general overview of the 2D material system covering some important aspects like growth, properties, stability, quality and its versatile applications are introduced. Number of growth methodologies have been explored in recent past and it become one of the most widely explored areas as per the large volume of literatures. Nevertheless large scale approach in CVD growth technique, monolayer formation have lot of other challenges such as control over defects, active edges, strain, allotropic phases and their stability etc. and are introduced in ***chapter 2 and chapter 3***. Chapter 2 describes the details of characterizing tools which are utilized for the analysis of 2D nanostructures. Defect and phase engineering have been actively explored in various 2D materials as they strongly influence their properties and applications to great extent. Enabling such control at atomic level during CVD growth has been explained in chapter 3 along with their significance for nanoelectronics and optoelectronic applications. We first focus on growth of material and then their further quality assurance. Sulfur evaporation rate controlled, screw dislocation driven (SDD) growth of two dimensional MoS_2 that contains unprecedented atomic step density has been presented in chapter 3. SDD growth of atomic thin MoS_2 on amorphous SiO_2 or crystalline and conducting Si substrate paves way to form spiral morphology of 2D materials without the need of single crystalline miscut substrates to initiate the line defects.

Chapter 4 describes the surface and interface engineering within 2D nanostructures (MoS_2, WS_2) in terms of their orientation, shape and structural confinement. Vertically and horizontally oriented growth have been explained in terms of their controlled growth environment and process parameters. Similarly, controlling microstructures of WS_2 during CVD growth has been demonstrated with aid of FESEM and TEM observations. Detailed mechanistic growth sequences from WO_3 nanorod to nanotube, monolayer and pyramidal 3D structures of WS_2 has been achieved using atmospheric pressure CVD. The active edges in vertically oriented MoS_2 layers have been tested for the enhanced hydrogen evolution and also, microstructural change based WS_2 has been studied for the active photo and gate modulated photo sensing performance.

Chapter 5 highlighted the point defect clustering driven, faceted void formations with luminescent enhancement at edges as well as surfaces in WS_2 monolayer during large scale CVD growth. We have used aberration-corrected scanning transmission electron microscope (AC-STEM) high angle annular dark field (HAADF) imaging to probe the atomic terminations of S and W to explain the observed luminescent enhancement in particular terminated edges. Defect generation and void growth dominate at later stages during CVD growth and provide optimum processing window for monolayer WS_2 as well as faceted void growth. Growth of faceted voids not only follow the geometry of monolayer facets but also show similar atomic terminations at the edges and thus enables local manipulation of photoluminescence intensity enhancement with an order of magnitude increment. Similarly, the implication of nanomanufacturing technique has been employed to generate patterned and modulated 2D monolayer materials. Such control over patterning in monolayers of WS_2 and MoS_2 aid the development of novel, miniaturized devices for nanoelectronics and nanophotonics applications. The site-specific nanosculpting of CVD grown WS_2 and MoS_2 monolayers achieved and spatially modulate PL intensity up to more than an order of changes. To analyze the systematic strain variation, relatively shallow indentations are also carried out with conical tip of ~5 μm radius. Raman and PL measurements carried out near indented region indicate the systematic variation in strain with respect to load and location. Further, nanosculpting to design non-periodic structures is achieved by performing nanoindentation close proximity to each other with detailed Raman and PL mapping.

Chapter 6 describes the phase engineering in 2D monolayer to overcome some of the fundamental limitations of conventional heterostructures. We have shown first time achievement of atmospheric pressure CVD grown coexisting polymorph (WS_2) in single domain monolayer WS_2 with uniform large scale upto 150 μm size. The coexisting polymorphs forming the seamless homojunction show unique optical and electrical behavior. Hexagonal single domain of WS_2 is organized in the alternate triangular heterophase such that 1H-1T and 1H-1T' coexisting phases are lying sidewise. AC-STEM has been used to identify the defect dominated structural polymorphic (1H-1T-1T') formation. Atomically thin heterophase formation in controlled growth with several featured challenging utilities provide unique platform for nanomanufacturing of 2D layers.

Chapter 7 describes the defects in atomic thin heterogeneous 2D materials that play major role to control and tune the electronic and optical properties. CVD enabled large scale growth of 2D materials with control over domain size, phase and defects to enhance the local properties that can be engineered during growth stage by varying process parameters suitably to design nanoscale materials and devices. We made uniformly nucleated defect sites onto atomic thin 2D monolayer WS_2. Uniform defect induced monolayer growth kinetics has been proposed with scalable CVD synthesis which provides the formation mechanism at constant thermodynamic condition. Uniformly decorated defects causing local luminescence enhancement mainly favored through S-deficiencies and confirmed by the X-ray photoemission spectroscopy. Spatially resolved PL and Raman spectral mapping depicts the homogeneous modulation as well as strain variation irrespective to the surrounding of defect rich region in monolayer domain.

Chapter 8 explored the challenges of mechanical reliability of nanoscale devices due to lattice and thermal mismatch strains. On contrary to conventional wisdom, our observations on CVD growth of WS_2 monolayer reveal the formation of heterophase, cancel competing thermal mismatch and lattice strains which stabilize crack free monolayer heterostructures while homophase WS_2 monolayer suffer from severe cracking. To shed light on this unique thermal strain relaxation in heterophase WS_2 monolayer, systematic investigation with aid of *in-situ* Raman spectroscopy has been carried out from 4K to near room temperature (330K). The measured thermal expansions of CVD grown heterophase WS_2 monolayers provides the tensile strain arising from thermal expansion mismatch, found to be cancelled by compressive lattice mismatch strain developed in heterophase WS_2 monolayer. Phase engineered WS_2 monolayer with differential thermal expansion of different polymorphic phases are relevant for the design of robust heterostructures based nanoscale devices. Similarly, electron beam lithography

(EBL) has been used to fabricate field effect transistor onto heterogeneous monolayer WS_2. Neighboring facet in single flake of heterophase domain has been used to measure the photo-induced current for different back-gate biased conditions. We observed nearly five times lesser drain current for semi-metallic phase (1T'), showing less electron–hole pair generation in compared with semiconducting (1H) phase, measured at same condition. In addition, rationalized photo-device utilization has been performed by making this heterophase into sub-nm thin channels or any arbitrary structures through the facile EBL patterned plasma etching process. Also, other arbitrary geometrical shapes have been fabricated using this facile technique to show the photo-device formation.

Finally, the overall findings on CVD growth, control of defect and co-existing phase formation along with the investigated optical, electrical and thermal properties are summarized with few indicators for further device development using atomically thin 2D materials.

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