Two-dimensional WS_2 layer in sensor application

Robert Andok[1], Katia Vutova[2, b)], Ivan Kostic[1, a)], Evgeniy Manoilov[2]
Institute of Informatics, Slovak Academy of Sciences, Dubravska cesta 9, 845 07 Bratislava, Slovak Republic[1]
Institute of Electronics, Bulgarian Academy of Sciences, 72, Tzarigradsko chaussee blvd., Sofia 1784, Bulgaria[2]
*E-mail: ivan.kostic@savba.sk [a)], katia@van-computers.com[b)]

Abstract: *This paper presents a study on the current state of research and use of dichalcogenides of transition metals, particularly WS_2. The properties of WS_2 in the context of its application in sensor technology and highlight the anticipated advantages of nanostructured disulfides are discussed.*

Keywords*: DICHALCOGENIDES OF TRANSITION METALS, TUNGSTEN DISULFIDE, GAS SENSOR, ELECTRON BEAM LITOGRAPHY*

1. Introduction

In the face of industrial globalization and population growth, the need for ultrasensitive and real-time monitoring of biological, chemical, and physical threats has become paramount. Nano-sensors are leading this new era, offering easy, rapid, sensitive, user-friendly, selective, and affordable solutions. The application of two-dimensional (2D) materials in sensors is expanding rapidly due to their unique properties, which stem from their inherent structures. These materials are being used in various fields, from environmental monitoring to healthcare, due to their exceptional ability to detect specific analytes and physical stimuli.

2D materials, such as graphene, transition metal dichalcogenides (TMDs), black phosphorus (BP), hexagonal boron nitride (h-BN), and MXenes, have garnered significant attention in detection and sensing strategies. The primary advantages of 2D materials include their high surface-area-to-volume ratio, which provides numerous reactive sites for interaction with analytes. Additionally, their conductivity can be finely tuned by controlling structural defects, layer numbers, doping, or post-functionalization. These materials are also compatible with state-of-the-art technologies due to their mechanical strength and flexibility. The exponential increase in publications on 2D materials for sensing highlights their great potential in this field. Their large surface area, enriched with active sites, enhances sensitivity and allows for ultra-low detection limits, making them ideal for various sensing applications.

Transition metal dichalcogenides (TMDs) have emerged as a promising class of 2D materials owing to their unique electronic, optical, and structural properties [1, 2]. TMDs exhibit diverse polymorphic structures, including the stable trigonal prismatic (2H) phase and the metastable octahedral (1T) phase, which give rise to distinct electronic characteristics ranging from semiconducting to metallic [3]. The ability to engineer the phase of TMDs has opened up new possibilities for their application in various fields, particularly in sensors [4]. Electron beam technology has proven to be a powerful tool for fabricating and modifying TMD-based devices, enabling the development of high-performance sensors [5].

Phase engineering of TMDs is crucial for tuning their electronic properties and optimizing their performance in sensing applications. Direct synthesis strategies, such as precursor selection, catalyst incorporation, temperature control, and alloying, have been successfully employed to obtain TMDs with desired phases [8, 9]. Additionally, post-synthesis phase transformation can be induced by external factors like ion intercalation and thermal treatment [10].

TMDs have shown great potential in various sensing applications, including gas sensors, biosensors, and photodetectors [11]. The high surface-to-volume ratio, unique electronic properties, and phase-dependent characteristics of TMDs make them ideal candidates for sensitive and selective sensing [12].

Electron beam technology has played a significant role in advancing TMD-based sensors. Electron beam lithography (EBL) enables precise patterning and fabrication of TMD devices with well-defined geometries and dimensions [13]. This level of control is essential for optimizing sensor performance and achieving high sensitivity and selectivity.

2. Electron beam lithography (EBL)

Electron beam lithography (EBL) is one of the few "top-down" methods in nanotechnology and it is becoming increasingly widespread in R&D and small volume production due to its flexibility and mask-less nature, very high (sub-10 nm) resolution and accuracy and in many cases EBL is the only possible alternative.

The ultimate resolution of electron beam lithography is not set by the resolution of electron optical systems, which can approach 0.1 nm, but by the resolution of the resist and by the subsequent fabrication process [14], therefore superior resists are crucial for the application of e-beam lithography and their performance determines the final results of the structures patterning.

Achieving sub-100 nm structures using EBL is a very sensitive process determined by various factors, starting with the choice of polymer resist material and ending with the development process. There is a large number of parameters affecting the EBL process in a complex, interacting fashion. The objective of manipulating these parameters is to achieve a high resolution, high quality, high throughput result with large process windows to maximize yield and reproducibility.

Commonly used electron beam resists are polymer materials such as poly-methyl-methacrylate (PMMA) [15]. In the last decade, there has been significant interest in the usage of an alternative inorganic electron beam resist hydrogen silsesquioxane (HSQ) with the chemical formula [HSiO3/2]2n [16]. HSQ (Dow Corning) is a negative tone resist which cross-links to form an insoluble silica-like structure. HSQ is used as a high-resolution resist with resolution down below 10 nm when using very small spot sizes and acceleration voltages of 100 keV [17 - 20]. On the other hand, as inorganic resist material, it is attractive material as a masking layer in reactive ion etching (RIE) because of selectivity in RIE is higher in comparison with polymer resists. High-contrast and high-resolution patterning in HSQ has numerous potential applications. For instance, quantum dots, large-area patterning of dot structures for the fabrication of high-density bitpatterned media, novel superconducting single-photon detectors [21, 22].

A powerful alternative in the throughput improving is Variable Shaped Beam (VSB) writing principle which can achieve considerably higher throughput than Gaussian spot beam tools. Variable shaped beam mask writers are currently the most commonly used tools. With VSB tools, EBL has made a number of advances in micro- and nano-devices possible [23]. An example of VSB lithography system is ZBA23 tool (Vistec Electron Beam, GmbH) [24]. In this tool, the rectangular shape size can be varied from 50 nm up to 3000 nm in steps of 50 nm. Accelerating voltage is optional 20 or 40 keV. The writing field, which is defined by the maximum deflection range of the electromagnetic deflection system, is 3x3 mm^2, divided into 0.2x0.2 mm^2 sub-fields by the fast electrostatic deflection system.

Moreover, electron beam irradiation has been utilized to induce local phase transitions in TMDs, allowing for the creation of heterophase structures with enhanced sensing capabilities [25]. By selectively converting regions of a TMD layer from the semiconducting 2H phase to the metallic 1T phase, it is possible to create high-quality electrical contacts and improve charge transport in the sensing device [26].

3. Tungsten disulfide (WS_2)

Tungsten disulfide (WS_2) is a notable 2D material used in sensing applications. WS_2-based sensors have shown high sensitivity and selectivity for detecting gases such as ammonia (NH_3) and nitrogen dioxide (NO_2). The material's n-type nature allows it to respond effectively to reducing gases like ethanol and NH_3, while its conductivity can be significantly affected by oxidizing gases like oxygen. WS_2 sensors can be fabricated using various methods, including electron beam technology, liquid exfoliation and chemical vapor deposition (CVD), and have demonstrated excellent performance in real-time sensing.

Electrical Properties of WS_2 : WS_2 exhibits unique electrical properties that make it a promising material for nanoelectronics, optoelectronics, and flexible devices. In case of monolayer WS_2 , direct bandgap is around 2.0 eV. In case of multilayer WS_2 , indirect bandgap is ~1.3–1.4 eV.

WS_2 exhibits moderate electron mobility (μ): Monolayer WS_2 : ~10–50 cm²/V·s (at room temperature), Few-layer WS_2 : ~50–200 cm²/V·s, Bulk WS_2 : ~400 cm²/V·s (comparable to Si) [27, 28].

Preparation of WS_2 : Tungsten Disulfide (WS_2) can be prepared using several methods. It depends on the desired application, structure (bulk, nanosheets, monolayers, etc.), and quality. Common preparation methods of 2D WS_2 monolayers or few-layer films for microelectronis and optoelectronics are Chemical Vapor Deposition (CVD) and Physical Vapor Deposition (PVD). In case of CVD, a tungsten precursor (e.g., WO_3 , WCl_6) and a sulfur source (e.g., S or H_2S) are reacted at high temperatures (600–900°C) [29, 30].

Synthesis of 2D (WS_2) using PVD like sputtering offer potential for large-area and controlled deposition, they are less commonly employed compared to CVD for WS_2 synthesis [31, 32].

4. WS_2 in gas sensors

The sensing mechanism of 2D MoS_2 and WS_2 depends on a gas-induced doping effect [33, 34]. The sensing materials may donate or take charges depending on the type of gases (oxidizing or reducing), which causes subsequent changes in sensor conductance in accordance, allowing the sensor to detect the presence of gas molecules [35, 36]. The sensing materials, on the other hand, may revert to their initial condition again when the sensor is exposed to air or pure nitrogen due to the desorption of gas molecules. Strong or weak interactions may develop due to variations in the adsorption energies of different types of adsorbates and absorbents. Theoretical research on the adsorption energy between a test gas molecule and a mono- or multilayer WS_2 found that polar gas molecules, such as NH_3 and NO_2, had higher adsorption energy than non-polar or weak polar ones, such as O_2, CH_4, and CO [37]. In addition, high adsorption energy typically affects gas sensing performance because the gas molecules will bind more strongly to the sensor, which potentially increases sensitivity as more molecules are detected [38, 39]. However, stronger adsorption energy may lead to slower recovery or desorption rates, which is not ideal in applications where rapid detection and clearance are critical. In summary, both the binding energy and the electron transfer will affect the performance of 2D material gas sensors [40].

5. Conclusions

TMDs have emerged as promising materials for the development of high-performance sensors due to their unique properties and phase-dependent characteristics. Electron beam technology has played a crucial role in advancing TMD-based sensors by enabling precise fabrication, patterning, and phase engineering. As research continues to progress, it is expected that the combination of TMDs and electron beam technology will lead to the development of novel sensing devices with enhanced sensitivity, selectivity, and reliability for a wide range of applications, promises to further expand the potential of TMDs in addressing global technological and environmental challenges.

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7. References

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