Characterization Methods Shaping the Future of 2D Materials in the Semiconductor Industry

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The integration of 2D materials into the semiconductor industry presents a paradigm shift, promising enhanced performance and efficiency in semiconductor devices. Graphene and Transition Metal Dichalcogenides (TMDs) stand out among these materials, offering unique properties suitable for various semiconductor applications. However, realizing their potential requires overcoming synthesis challenges and ensuring precise characterization. This article explores the role of characterization and wafer inspection methods in shaping the future of 2D materials in the semiconductor industry. It discusses synthesis techniques compatible with their scale up and highlights the current challenges such as uniformity, and defect minimization. The article also focuses on the key characterization properties, thus emphasizing the importance of techniques like Raman spectroscopy and Photoluminescence (PL) spectroscopy, crucial for the successful integration of 2D materials in the semiconductor technology.

Key words
2D materials, semiconductor industry, Chemical Vapor Deposition (CVD), Raman spectroscopy, Photoluminescence (PL) spectroscopy

Introduction

The world of semiconductors is constantly evolving, and one of the most exciting developments in recent years is the emergence of 2D materials. Among the pioneers in this field is graphene, a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice. Graphene exhibits remarkable properties, such as high electrical and thermal conductivity, exceptional mechanical strength, and extraordinary electron mobility. Alongside graphene who by nature is semi-metallic, Transition Metal Dichalcogenides (TMDs) have gained attention for their band gap, making them suitable for semiconductor applications (Figure 1). Moreover, other 2D materials like h-BN, black phosphorous, and MXenes have also demonstrated promising characteristics. The unique properties of 2D materials open up a myriad of potential applications. These materials hold great promise in energy storage devices, sensors for various industries, optical lighting technologies, healthcare biosensors, photovoltaics, and electronics, including transistors and memories. This article explores the potential of these materials in the semiconductor industry and the characterization and inspection methods that are helping their integration.

Roadmap and Scaling Techniques

In the semiconductor industry, the technology roadmap has been guided by Moore‘s Law, with a focus on miniaturization and integration of components on silicon chips. However, as traditional scaling approaches face limitations, the introduction of 2D materials offers a new dimension to continue progress. Happy scaling involved reducing the size of transistors to maintain performance, but heterogeneous scaling now introduces new materials with unique properties to improve overall performance and energy efficiency Figure 2[1]. 2D materials present exciting prospects for both front-end-of-line (FEOL, i.e. all the process steps that are related to the transistor itself)

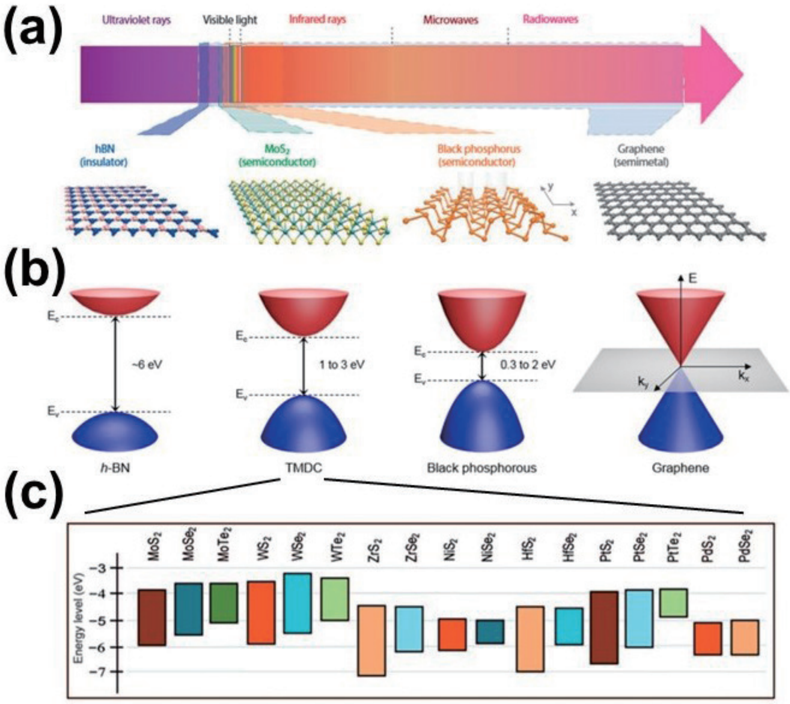

Figure 1 Optical response and electronic bandgaps of typical 2D materials. (a) Energy spectrum of various two-dimensional (2D) materials and their atomic crystal structures. (b) Electronic band structures of hexagonal boron nitride (*h*-BN), transition metal dichalcogenides (TMDCs), black phosphorous, and graphene. (c) Energy level diagrams of selected semiconducting TMDCs.

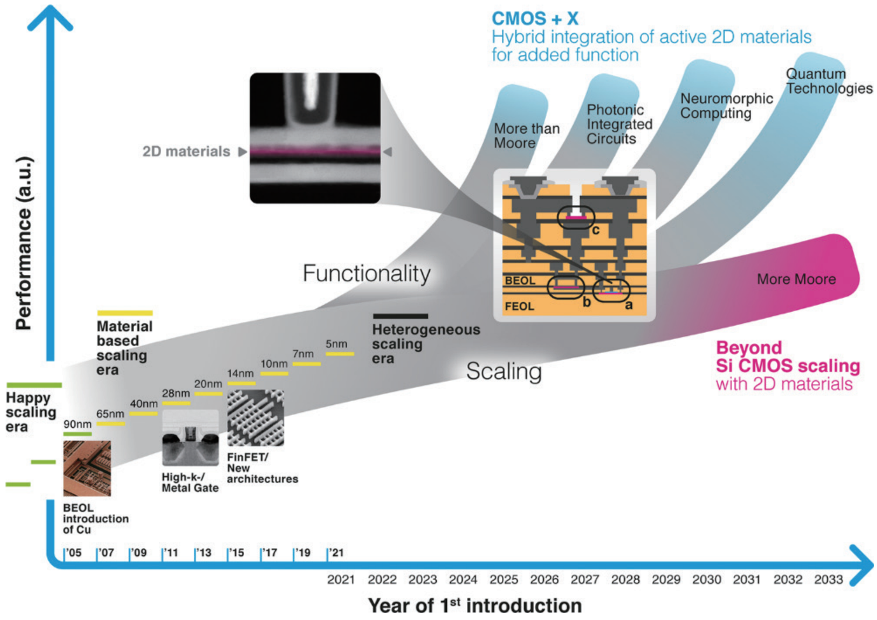

Figure 2 The era of geometrical scaling of silicon technology ended around the turn of the century (green lines, “happy scaling”). Since then, material and architecture innovations like copper interconnects, high-*k* dielectrics with metal gates and FinFETs continued to drive Moore’s law (yellow lines, “less happy scaling”). Future scaling, or “More Moore”, may require thin nanosheet transistors, where 2D materials are considered ideal candidates (magenta, inset a and transmission electron micrograph). Reproduced with permission from Lemme, M.C., Akinwande, D., Huyghebaert, C. *et al.* 2D materials for future heterogeneous electronics. *Nat Commun* 13, 1392 (2022) Figure 1.

and back-end-of-line (BEOL, i.e. the interconnects between the transistors are formed within a device) applications.

In FEOL, TMDs possess exceptional carrier mobility and bandgap properties, making them suitable candidates for next-generation transistors. These 2D materials can potentially replace traditional silicon-based transistors, leading to faster switching speeds, reduced power consumption, and increased device performance. In BEOL, as integrated circuits become smaller and more complex, interconnects play a vital role in ensuring efficient signal transmission. Graphene with high electrical conductivity and low resistivity can be utilized as interconnect materials, reducing signal delay and enhancing overall chip performance. Still in BEOL, barrier layers are used to protect underlying layers from diffusion and contamination. Hexagonal Boron Nitride (h-BN), known for its excellent dielectric properties, can serve as an ideal barrier material to protect sensitive components in the semiconductor device.

Synthesis Challenges and Methods

Efficient synthesis methods are essential to harness the potential of 2D materials for semiconductor applications. Two main approaches commonly employed in the synthesis of these materials are the top-down approach and the bottom-up approach. The top-down approach involves exfoliating bulk materials to obtain 2D layers. The most well-known example of this approach is the exfoliation of graphite to produce graphene layers. While this method provides a starting point for research and small-scale applications, the scalability and precise control provided by the bottom-up approach with Chemical Vapor Deposition (CVD) make it a leading contender for large-scale commercial production of 2D materials. Indeed, CVD (and its variant MOCVD, Metal-Organic Chemical Vapor Deposition) offers several advantages over the top-down approach, including better scalability to large wafers, the control over layer thickness, and the possibility to easily change the precursors for the growth of heterostructures. However, it also presents its own set of challenges:

a. Precursor Selection: Choosing the appropriate precursor gases is critical to achieving high-quality 2D materials. The selection influences the growth rate, crystallinity, and defect density of the synthesized layers.

b. Substrate Compatibility: The choice of substrate plays a crucial role in CVD synthesis. Different 2D materials require specific substrates with matching lattice constants and thermal properties to ensure successful growth and adhesion. For instance, when growing graphene using CVD, copper foils or nickel foils are often used as substrates. The carbon atoms in graphene align with the lattice structure of the metal substrate during the growth process, promoting the formation of a single-layer graphene with good adhesion to the substrate. Similarly, in the growth of TMDs like molybdenum disulfide (MoS_2), sapphire substrates are frequently utilized due to their close lattice match with the TMD material, facilitating high-quality growth. In both cases, the choice of substrate with appropriate lattice constants and thermal expansion coefficients helps to minimize strain and defects during the growth process, resulting in high-quality 2D materials that are well-suited for subsequent integration into semiconductor devices.

c. Uniformity and Defects: Achieving uniform and defect-free 2D layers across a large-area wafer is a significant challenge in CVD. Factors like temperature, gas flow rates, and reaction time must be precisely controlled to minimize defects and ensure uniform growth.

d. Transfer and Stacking: Once the 2D material is synthesized on a growth substrate, it needs to be transferred from the initial growth substrate onto the desired semiconductor device substrate while maintaining its structural integrity. The choice of the target substrate depends on the specific application and requirements of the semiconductor device. For instance, if the 2D material is intended for FEOL applications, it may be transferred onto a silicon wafer. Integrating the 2D material onto a silicon substrate enables compatibility with existing silicon-based processes current used in semiconductor fabs. On the other hand, in BEOL applications, the target substrate might include various insulating or conducting materials, depending on the intended use of the 2D material. For example, if the 2D material is to be used as a barrier layer or interconnect, it might be transferred onto an insulating material like silicon dioxide (SiO_2) or a conducting material like copper.

The transfer process itself can be delicate and challenging, as it involves peeling the 2D material off the growth substrate and carefully placing it onto the target substrate. Techniques such as dry transfer, wet transfer, and polymer-assisted transfer play a crucial role in the successful integration of 2D materials into semiconductor devices. These methods are employed to preserve the crystalline quality of the 2D material, cover as large an area as possible, and prevent doping from contamination and defects like wrinkles and cracks.

Overcoming the challenges associated with CVD synthesis methods is of paramount importance to fully harness the potential of 2D materials in the semiconductor industry and facilitate the development of innovative and high-performance devices. To this end, current efforts are being directed towards directly growing 2D materials on silicon or silicon dioxide substrates. This approach offers significant advantages, including streamlining the device fabrication process.

Characterization Techniques for 2D Materials in Semiconductor Applications

As the potential applications of 2D materials continue to expand and are becoming concrete on the market, the semiconductor industry is taking notice. Leading manufacturers of deposition systems are investing in R&D to meet the growing demand, and new deposition systems that enable their synthesis on large wafers are emerging on the market. Meanwhile, major players in the semiconductor industry are exploring actively the possibility to incorporate 2D materials into their next-generation devices. To ensure the successful integration, precise and reliable characterization techniques are essential to check the quality and uniformity of 2D materials.

Characterization encompasses the growth optimization of the 2D materials on template wafers and the quality of the materials after transfer. Several key parameters are of interest (in brackets the main techniques used):

- Thickness and number of layers (Raman spectroscopy, AFM (Atomic Force Microscopy), Reflectometry, Ellipsometry)

- Crystalline quality (Raman spectroscopy)

- Band Gap and stress (Raman spectroscopy and Photoluminescence)

- Carrier concentration and doping level (Raman spectroscopy and Photoluminescence)

- Identification and quantification of defects (point defects, but also cracks, wrinkles, grain boundaries and holes) or contaminants (polymeric, metallic) (Raman spectroscopy and Photoluminescence, AFM)

Indeed, Raman spectroscopy is extensively used for characterizing graphene. Figure 3 illustrates the Raman map of graphene on a 4” sapphire wafer. The Raman spectra of graphene are characterized by three main bands referred to as the G, 2D-bands, and the D-band which appears in the presence of defects within the carbon lattice[2]. Histograms of Raman parameters present the distributions of (upper) the Full Width at Half Maximum (FWHM) of the 2D band, (middle) the D/G intensity ratio, and (bottom) the 2D/G intensity ratio. These Raman parameters respectively provide insights into the crystalline quality (2D FWHM ~ 40 cm^{-1} for graphene grown on pristine sapphire), the defect density (low value is a D/G ratio of ~ 0.13)[3-4], and the doping level through the charge carrier concentration (2D/G ratio ~1.80 for grown graphene on pristine sapphire, carrier concentration estimated to be around 5×10^{12} cm^{-2})[5] and the layer thickness[6].

For 2D Transition Metal Dichalcogenides (TMDs), Raman and Photoluminescence (PL) spectroscopy are particularly useful in determining the number of layers[7-9], stoichiometry[10], carrier density[11-12] and the presence of defects[4]. Figure 4 shows Photoluminescence and Raman maps of tungsten disulfide (WS_2), a member of the 2D TMD family, on a 12” Si wafer. The Photoluminescence spectra are primarily characterized by exciton and trion bands, and their intensity ratio enables differentiation between various regions based on charge carrier concentration[13]. The Raman spectra of WS_2 exhibit prominent peaks: E2g (in-plane mode) and A1g (out-of-plane mode)[14]. The

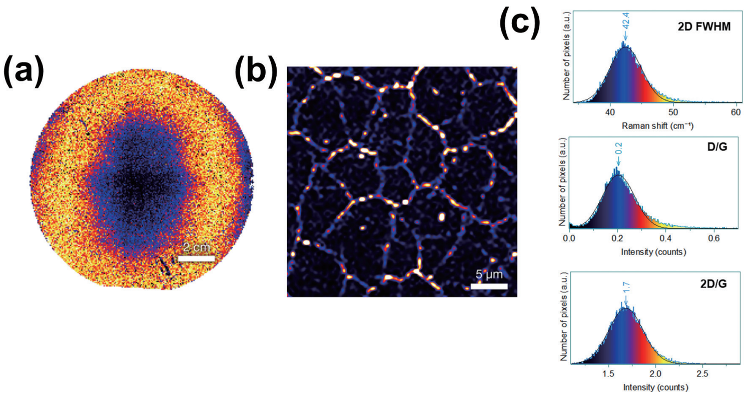

Figure 3 (a) Raman map of graphene on a 4” sapphire wafer, (b) high resolution Raman image on defects, (c) Histograms of Raman parameters (Full Width at Half Maximum (FWHM) of the 2D band, D/G intensity ratio, and 2D/G intensity ratio).

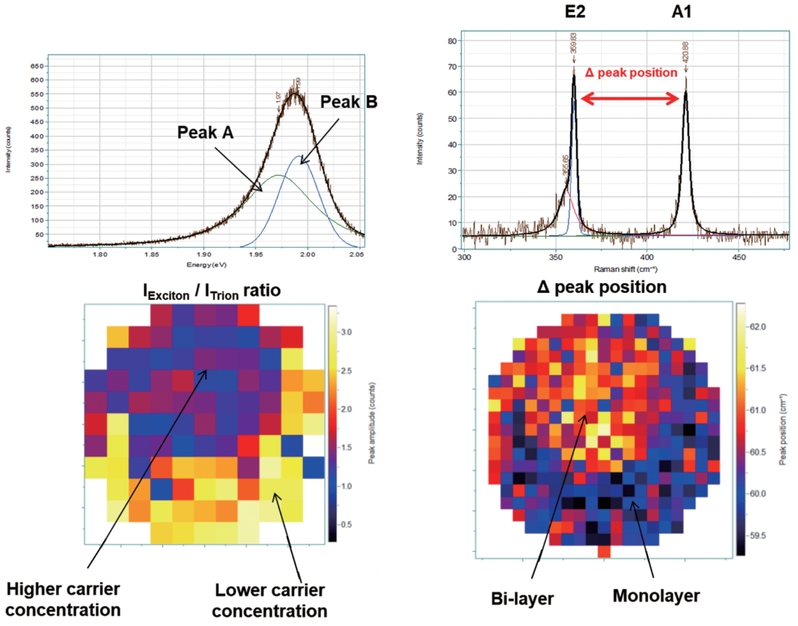

Figure 4 Photoluminescence (left) and Raman maps (right) of tungsten disulfide (WS_2) on a 12” Si wafer.

Figure 5 HORIBA LabRAM Odyssey Semiconductor. Photoluminescence and Raman imaging on wafers up to 300 mm diameter for 2D materials wafer uniformity assessment and defects inspection.

frequency difference between these two Raman bands directly correlates with the number of layers of the 2D materials.

Both techniques, Raman and Photoluminescence, can be used on the same instrument for wafer imaging, offering insights into the distribution and quality of 2D materials over large areas (Figure 5).

Conclusion

The advent of 2D materials has opened new possibilities for the semiconductor industry. Graphene and TMDs hold immense promise for both FEOL and BEOL applications, paving the way for more efficient, compact, and powerful semiconductor devices. However, significant challenges remain in the synthesis, transfer, and integration of 2D materials. For the compatibility with fabrication rules and successful integration on 300 mm flows, substantial efforts focus on defect reduction and large-scale deposition, emphasizing the need of efficient characterization techniques. HORIBA offers solutions tailored for this industrial research with Raman and PL imaging systems designed for full wafer imaging. Nevertheless, as progress continues, the demand for rapid online metrology is growing and collaborations between semiconductor players and HORIBA have already begun for the development of new in-line metrology systems. Now is the time to replicate in fab the high quality 2D materials demonstrated in the lab. If we get there, 2D materials are expected to play a pivotal role in shaping the future of semiconductor technology.

* Editorial note: This content is based on HORIBA's investigation at the year of issue unless otherwise stated.

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