Applications of MoS₂ as a Two-Dimensional Material Beyond Graphene

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1. Introduction & Beginnings

- (a) Before graphene
 - i. Prior to the mid-1980s (1985) graphite had been used for several practical applications [16]. In 1985 the discovery of fullerenes (C₆₀) initiated the postualtion of the interesting and beneficial properties of the structure and its derivatives, assuming that it could be synthesized in large amounts [12].
 - ii. Theories suggested the possibility of one-dimensional structures of this form, and carbon nanotubes (1991) [9]. This suggested the possibility of synthesizing carbon structures on a larger scale than was previously possible with fullerenes.
 - iii. With the semiconductor industry approaching the limits of improvements that could be achieved by using mainly silicon. As a result, this spurred the search for new alternative materials. Examples include organic conductors [17, 4] and carbon nanotubes [2]. The primary goal of which, to extend the use of the field effect of metals. For example, the main idea would be to translate metallic transistors developed to a much smaller size that would consume less energy and operate at higher frequencies than current semiconductor devices [17, 20].
 - iv. In 2004 single layers of graphite were isolated by Geim et. al [17, 18]. They observed field effects in an atomically thin layer of graphene. They prepared the sample using exfoliation (define later in synthesis methods section). At the time, it was the leading candidate for metallic transistors and other electronic components. As a result, this began a breadth of research on graphene.
- (b) After Graphene: Emergence of other 2D materials
 - i. Aside from graphene, there has been development of other 2D inorganic materials.
 - ii. The properties of 2D crystals have been met with great interest among the contemporary semiconductor industry and other similar fields [1].

2. Properties of 2D materials compared to graphene

- (a) Properties of Graphene
 - i. Graphene is made of a single layer of C atoms in 2D honeycomb lattice. It is the fundamental piece of graphite (3D), 1D carbon nanotubes and 0D fullerenes [22].
 - ii. Some of graphene's important properties are:
 - A. High surface area [22]
 - B. High Young's Modulus [22]
 - C. Good thermal conductivity
 - iii. Graphene's proposed and some forseen applications are:
 - A. High speed electronics [14].
 - B. Optical devices [15].
 - C. Energy applications [15, 11, 24].
 - D. Hybrid Materials and Chemical sensors [15, 6, 23, 8].

3. Why are 2D materials significant?

- (a) TMDs
 - i. Transition metal dichalcogenides (TMDs)

- ii. Hexagonal layers of metal atoms (M) between two layers of chalcogen atoms (X) with a MX₂ stoichiometry. [22].
- iii. Different TMDs are possible. It is dependent on the combination of the chalcogen (i.e. S, Se, or Te) and a transition metal (i.e. Mo, W, Nb, Re, Ni, or V) [21, 22].
- (b) As opposed to pristine graphene (with a zero band gap) and the band gap of around a few hundred meV introduced from bilayer graphene to nanoribbons, a single-layer MoS₂ sheet is a direct band gap semiconductor [22].
- (c) MoS₂ transistor on/off ratio for single layer is $\sim 10^8$ at room temperature, this ratio is about 100 times higher than graphene [22, 17].
- (d) Many 2D materials are promising, perhaps most promising for integration into digital circuits is MoS₂.

4. Synthesis Methods

- (a) Exfoliation
 - i. Early methods, such as micromechanical exfoliation [16, 3].
 - ii. Micromechanical exfoliation is the best method for separating layered TMD crystals. Much of the characteristics demonstrated by FETs are derived from mechanically exfoliated MoS₂ sheets [22].
- (b) Surface assisted in Situ Growth
- (c) Exfoliation into colloidal solutions

5. Imaging and Detection Techniques

- (a) TERS: near field tip-enhanced Raman spectroscopy. Utilitzes an AFM or STM that is coated with Au or AG to enhance the local Raman spectra. Used to detect defects and grain boundaries [3].
- (b) X-ray Diffraction: can provide unit cell information [3].
- (c) FQM: Flourescene quenching microsopy. [3].
- (d) AFM: used to determine layer thickness up to 5% precision [3, 7, 19].
- (e) STM: Scanning tunneling microscopy. A probing based technique that can measure electronic and topographic properties of single-atom materials.
- (f) TEM: Transmission electron microscopy. Provides details of layer sizes, stacking relationships, and composition [3].

6. State-of-the-art

(a)

7. Problems & Outlook

- (a) Problems that need to be addressed:
 - i. A method is needed to control instrinic doping methods [13].

Possible solutions include:

Introducing substitution atoms of the lattice during growth [5].

- ii. How to make good electrical contacts with MoS₂. [13]
- iii. According to theory, the charge carrier mobility should be able to be improved by a significant factor [13, 10].
- (b) Outlook:

i.

References

- [1] Deji Akinwande, Nicholas Petron, and James Hone. Two-dimensional flexible nanoelectronics. *Nature Communications*, 5, 2014.
- [2] Ray H. Baughman, Anvar A. Zakhidov, and Walt A. de Heer. Carbon nanotubes—the route toward applications. Science, 297(5582):787–792, 2002.
- [3] Sheneve Z. Butler, Shawna M. Hollen, Linyou Cao, Yi Cui, Jay A. Gupta, Humberto R. Gutirrez, Tony F. Heinz, Seung Sae Hong, Jiaxing Huang, Ariel F. Ismach, Ezekiel Johnston-Halperin, Masaru Kuno, Vladimir V. Plashnitsa, Richard D. Robinson, Rodney S. Ruoff, Sayeef Salahuddin, Jie Shan, Li Shi, Michael G. Spencer, Mauricio Terrones, Wolfgang Windl, and Joshua E. Goldberger. Progress, challenges, and opportunities in two-dimensional materials beyond graphene. ACS Nano, 7(4):2898–2926, 2013. PMID: 23464873.
- [4] C.D. Dimitrakopoulos and D.J. Mascaro. Organic thin-film transistors: A review of recent advances. *IBM Journal of Research and Development*, 45(1):11–27, Jan 2001.
- [5] Kapildeb Dolui, Ivan Rungger, Chaitanya Das Pemmaraju, and Stefano Sanvito. Possible doping strategies for mos₂ monolayers: An ab initio study. Phys. Rev. B, 88:075420, Aug 2013.
- [6] Maher F. El-Kady, Veronica Strong, Sergey Dubin, and Richard B. Kaner. Laser scribing of high-performance and flexible graphene-based electrochemical capacitors. Science, 335(6074):1326–1330, 2012.
- [7] Katsutoshi Fukuda, Kosho Akatsuka, Yasuo Ebina, Renzhi Ma, Kazunori Takada, Izumi Nakai, and Takayoshi Sasaki. Exfoliated nanosheet crystallite of cesium tungstate with 2d pyrochlore structure: Synthesis, characterization, and photochromic properties. ACS Nano, 2(8):1689–1695, 2008.
- [8] A. K. Giem and K. S. Novoselov. The rise of graphene. Nature Materials, 6:183–191, 2007.
- [9] Sumio Iijima. Helical microtubules of graphitic carbon. Nature, 354:56–58, 1991.
- [10] Kristen Kaasbjerg, Kristian S. Thygesen, and Antti-Pekka Jauho. Acoustic phonon limited mobility in twodimensional semiconductors: Deformation potential and piezoelectric scattering in monolayer mos₂ from first principles. Phys. Rev. B, 87:235312, Jun 2013.
- [11] Keun Soo Kim, Yue Zhao, Houk Jang, Sang Yoon Lee, Jong Min Kim, Kwang S. Kim, Jong-Hyun Ahn, Philip Kim, Jae-Young Choi, and Byung Hee Hong. Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature*, 457:706–710, 2009.
- [12] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley. C60: Buckminsterfullerene. *Nature*, 318:162–163, 1985.
- [13] Dominik Lembke, Simone Bertolazzi, and Andras Kis. Single-layer mos2 electronics. *Accounts of Chemical Research*, 48(1):100–110, 2015. PMID: 25555202.
- [14] Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and Ph. Avouris. 100-ghz transistors from wafer-scale epitaxial graphene. *Science*, 327(5966):662, 2010.
- [15] M. Liu, X. B. Yin, E. Ulin-Avila, B.S. Geng, T. Zentgraf, L. Lu, F. Wang, and X. Zhang. A graphene-based broadband optical modulator. *Nature*, 474:64–67, 2011.
- [16] Ruben Mas-Balleste, Cristina Gomez-Navarro, Julio Gomez-Herrero, and Felix Zamora. 2d materials: to graphene and beyond. *Nanoscale*, 3:20–30, 2011.
- [17] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov. Electric field effect in atomically thin carbon films. *Science*, 306(5696):666–669, 2004.
- [18] K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim. Two-dimensional atomic crystals. Proceedings of the National Academy of Sciences of the United States of America, 102(30):10451–10453, 2005.
- [19] Minoru Osada, Genki Takanashi, Bao-Wen Li, Kosho Akatsuka, Yasuo Ebina, Kanta Ono, Hiroshi Funakubo, Kazunori Takada, and Takayoshi Sasaki. Controlled polarizability of one-nanometer-thick oxide nanosheets for tailored, high- nanodielectrics. Advanced Functional Materials, 21(18):3482-3487, 2011.

- [20] Slava V. Rotkin and Karl Hess. Possibility of a metallic field-effect transistor. Applied Physics Letters, 84(16):3139–3141, 2004.
- [21] J.A. Wilson and A.D. Yoffe. The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Advances in Physics*, 18(73):193–335, 1969.
- [22] Mingsheng Xu, Tao Liang, Minmin Shi, and Hongzheng Chen. Graphene-like two-dimensional materials. *Chemical Reviews*, 113(5):3766–3798, 2013. PMID: 23286380.
- [23] Xi Yang, Mingsheng Xu, Weiming Qiu, Xiaoqiang Chen, Meng Deng, Jinglin Zhang, Hideo Iwai, Eiichiro Watanabe, and Hongzheng Chen. Graphene uniformly decorated with gold nanodots: in situ synthesis, enhanced dispersibility and applications. *J. Mater. Chem.*, 21:8096–8103, 2011.
- [24] Yanwu Zhu, Shanthi Murali, Meryl D. Stoller, K. J. Ganesh, Weiwei Cai, Paulo J. Ferreira, Adam Pirkle, Robert M. Wallace, Katie A. Cychosz, Matthias Thommes, Dong Su, Eric A. Stach, and Rodney S. Ruoff. Carbon-based supercapacitors produced by activation of graphene. *Science*, 332(6037):1537–1541, 2011.