

Thin Film Performance Optimization through Chemical Vapor Deposition

Andre Slonopas and Nibir K. Dhar

*U.S. Army Night Vision and Electronic Sensors Directorate,
Fort Belvoir, VA 22060*

Herbert Ryan

Bitome, Inc., 90 Forest Hills Street Unit 3, Boston, MA 02130

Pamela Norris

*Department of Mechanical and Aerospace Engineering, University of Virginia
Charlottesville, VA 22902*

Ashok K. Sood

*Magnolia Optical Technologies, Inc., 52-B Cummings Park, Suite 314,
Woburn, MA 01801*

Abstract

The broad applicability of chemical vapor deposition has made it a ubiquitous method to grow thin films; consequently, increasing publications on the topic. The most attractive feature of the chemical vapor deposition is its applicability for industrial sized projects. Notably, the film growth costs scales inversely with the processing batch size. This relationship is achieved while simultaneously preserving desirable opto-electrical properties in chemical vapor deposited materials. Furthermore, recent research has shown that it is possible to efficiently tune film performance by changing the deposition parameters and growth mechanisms. This work attempts to review the progress that has thus far been achieved in thin film optimization through chemical vapor deposition.

Keywords: Chemical Vapor Deposition, performance optimization, perovskites, graphene, electrical properties

INTRODUCTION

Advances in semiconducting thin film processing have laid the foundation for the exponential growth experienced in personal computing and related tech sectors over the past half century. In addition to the consumer market, semiconducting thin films find applications in defense, space exploration, atmospheric studies, optical systems, private, and commercial products.. To some extent, every piece of electrical technology, hardware, gadgetry, energy generation and storage, and commercial device operates as a result of thin film technology. The ability to sustain the same rate of technological innovation is largely dependent on our ability to scale thin film growth manufacturing and efficiently optimize their performance.

Recently, chemical vapor deposition has emerged as an effective method for depositing desirable organic, inorganic, and organo-metallic thin films. CVD method has been successfully used to deposit graphene, organo-halide perovskites, diamonds, transparent conducting oxides (TCO), and numerous other materials [1] [2] [3] [4] [5] [6] [7]. Furthermore, Murakami et al demonstrated that chemical vapor deposition is an effective tool for the optimization of film performance [6]. This discovery spurred research to elucidate the correlation between film deposition parameters and performance [8] [9] [10]. CVD has also been used for device manufacturing through methodological film layer deposition [11].

Film thickness and the grain size adjoining sample edges show uniformity and conformity across the sample [12]. Moreover, pre-deposition distillation allows deposition of film with various doping content or purity. This allows for the assembly of monolithic shapes and features with high aspect ratios for a broad range of device applications. All of these factors combined empower the user to manufacture and optimize on the mesoscopic scale, expanding the limits of technology application. The importance of the CVD as an enabling process technology cannot be overstated.

More recent advancements with individual CVD materials cannot be fully described with the detail deserved in a single review paper. Thus, this paper intends to cover only the recent high impact breakthroughs in CVD thin films and device optimization. Some of the current limitations of the process technology are also addressed. Several materials are discussed throughout this monographs many characteristics are homologous across all CVD films.

Theoretical Considerations

Numerous parameters play a role in chemical vapor deposition. As an example, the deposition rates and mechanisms are effected by the shape of the substrate, chamber type, size of the reactor, gas flow rate, chemical arrangements, and chemical compositions. Complicated and creative reaction schemes, involving high temperature decompositions, redox reactions, disproportionation, hydrolysis, or some combination of each may be required [13]. Despite a seemingly endless number of deposition parameters to optimize, in general, the film growths are achieved through a sequential process: i) The reagents are added to the substrate first. This creates an initial kinetic barrier. ii) Next gases are diffused through the barrier for the initial absorption on the

substrate surface. This is followed by the reactions of the chemical constituents and nucleation. From the above discussion it should be obvious that much variability in CVD films may exist. Hence deliberate thought on each chemical reaction is a necessity.

In an effort to simplify the mathematical analysis, laminar gas flow is assumed inside the chamber. Such an assumption is reasonable, since the high Reynolds numbers will never be reached at the short distances the gas traverses. Further the gas velocity at the substrate is assumed to reach zero. The gases are assumed to be a constant speed at some distance above the substrate, and the velocity decreases linearly from this constant value to the substrate. Utilizing these assumptions, the Boundary Layer Theory (BLT) may be used for the study of reaction dynamics [14]. The BLT method coupled with the simplifying assumptions mentioned above, enables concatenation of the chemical and mass transport processes on the heated surface to the gas flow. Thus, the Gibbs free energy equation is used to model the chemical nucleation in CVD films,

$$\Delta G = \sum_{i=1}^{\#products} \Delta G_{products} - \sum_{i=1}^{\#reactants} \Delta G_{reactants} \quad (1)$$

The change in Gibbs free energy, ΔG , is related to the equilibrium constant k_p

$$\Delta G = 2.3RT \log(k_p) \quad (2)$$

In theory the CVD process involves solely gases, thus the equilibrium constant relates to the sum of the partial pressures of the reactants and products. From solid state physics, the molar concentrations, and not the partial pressures, of the constituents are of interest. From the ideal gas law, the Gibbs free energy equation becomes [15].

$$\Delta G = \sum_{i=n_g}^g \left[n_g \Delta G_g + RT \ln(P) + 2T \ln \left(\frac{n_g}{N_g} \right) \right] + \sum_{i=1}^s n_s \Delta G_s \quad (3)$$

where n_g and n_s , are the molar concentrations of the reagents in the gaseous and solid states, respectively. N_g is the total molar concentration of all gaseous components. P and T are the total pressure and temperature, respectively. ΔG_g and G_s are the free energy of nucleation at specific temperatures for the gaseous and solid species, respectively. This equation has numerical solution for the free energy minima. The minimum free energy signifies the point at which the crystallization commences. It should also be evident that the nucleation commencement can be offset by the reagent concentrations, pressure or temperature.

From the purely theoretical perspective, the high reagent concentrations will induce film growth even at low pressures and temperatures (i.e. atmospheric conditions or STP). This means that nucleation can be forced at low temperatures making this

technique ideal for the growth of organic semiconductors. However, the temperature cannot be low to the point of condensation.

Considering the above discussion, reliable prediction of film performance and control of the deposition techniques in a CVD chamber is a daunting task. Carrier mobilities, resistivity, diffusion lengths, are all functions of grain sizes, layers compositions, porosities, contaminants, substrates, bond lengths and a plethora of other factors [16] [17] [18]. The inability of atomistic level simulations to predict film performance further highlights the difficulty of control in a stochastic system [19] [20].

EXPERIMENTAL DATA

Experimental studies of methane-deuterium interactions show low vapor temperature depositions result in symmetric scattering of clusters $\sim 10 \mu\text{m}$ in diameter [21]. These clusters tend to form in the bulk of the gas and coagulate into structures on the substrate. It is possible, therefore, to introduce various dopant elements to the films during the coagulation of structures on the substrate. The final structure depends upon the thermal properties of the material [6]. The low thermal diffusivity in organic materials forces a cluster-by-cluster deposition mechanism analogous to epitaxial growth. This results in high quality, largely defect free, firm crystalline structure to form that is optimal for opto-electronic devices, see Figure 1.

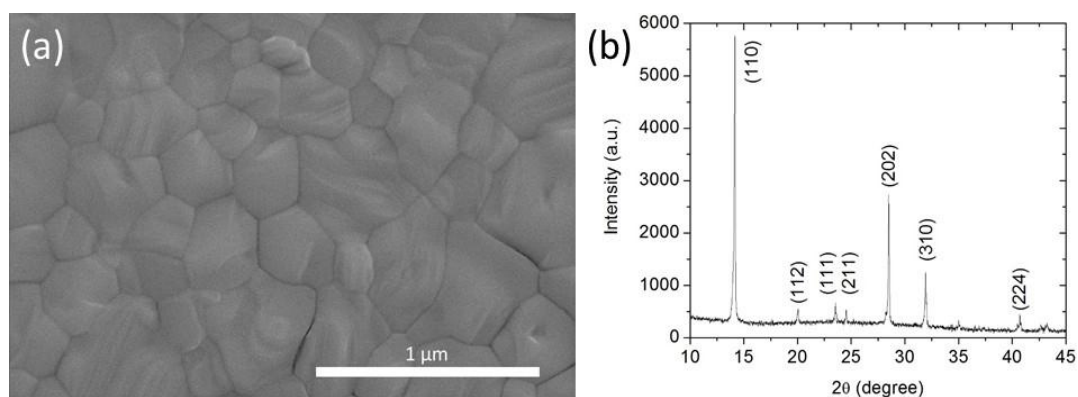


Figure 1. (a) SEM and (b) X-ray diffraction pattern of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite thin films.

Film properties and characteristics can be further tuned through the control of reagent concentration and the deposition atmosphere composition. Figure 2 shows the effects of reagent concentrations and atmospheric pressure on the current-voltage characteristics of a simple graphene-perovskite device. A noticeable shift in the location of the current minima is observed with a decrease in deposition pressure. This is mainly due to a decrease in contaminant interstitial trapping in films at low pressure atmospheres [22]. Furthermore, low atmospheric pressures tend to produce more ordered films; further changing the opto-electric performance of the films [22]. A significantly larger shunt resistance of the high deposition pressure films is also

observed. Shunt resistance is known to be caused by defects within the film. This is in agreement with the previous discussion.

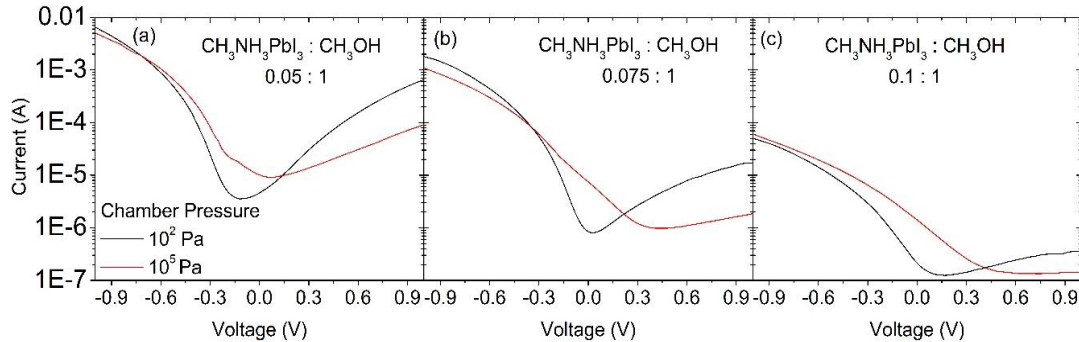


Figure 2. The I-V characteristics of CVD deposited graphene-perovskite device as a function of $\text{CH}_3\text{NH}_3\text{PbI}_3:\text{CH}_3\text{OH}$ concentration and deposition pressure.

Figure 2 details the changes observed in electrical performance as a consequence of adjusting $\text{CH}_3\text{NH}_3\text{PbI}_3 : \text{CH}_3\text{OH}$ ratios. An improvement in the current properties of these simple devices is observed at lower perovskite to methanol concentrations. The methanol is only the diluting medium and does not react with PbI_2 on the substrate. Thus, low $\text{CH}_3\text{NH}_3\text{PbI}_3$ concentrations allow for a more uniform distribution of the material within the diluent. Slow, uniform, and high quality epitaxial growth is expected. Favorable electrical behavior is seen in Figure 2 and attributed to the slow controlled material growth.

Additional studies further validate the link between reagent concentration and film performance. One such study highlighted below, explores the behavior of graphene deposited under various conditions. Previously, it was reported that graphene deposited under high reagent concentrations showed high disorder [23]. Raman analysis of graphene grown under various methanol concentrations is shown in Figure 3.

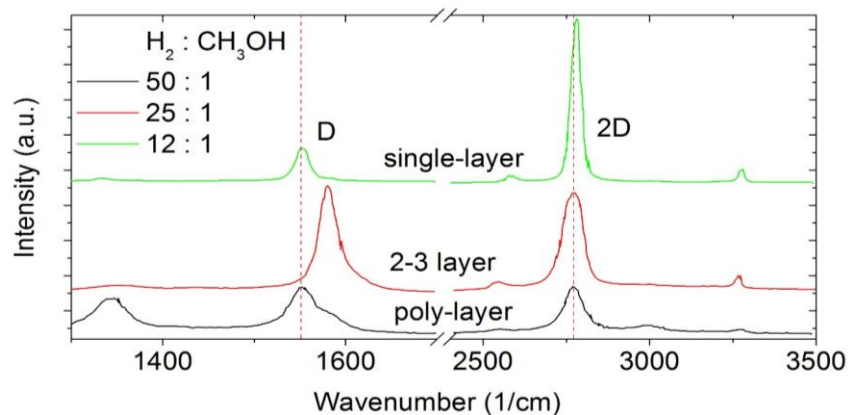


Figure 3. Raman spectra for the CVD grown graphene under various CH_3OH concentrations.

Raman analysis reveals formations of the D and 2D peaks at ~ 1550 and ~ 2750 cm^{-1} , respectively. A noticeable shift in the location of the peaks is also observed, indicating the formation of additional layers [24]. Additionally, a significant increase in the 2D peak intensity is observed. This increase is indicative of the disorder increase, typical of poly-crystalline and poly-layered films [25]. The disorders are largely a result of layer and lattice mismatches in films, thus forcing anharmonic phonon – free carrier interactions [26]. These results further validate the above discussion of epitaxially grown uniform films resulting from higher diluent concentrations in CVD. There is an ongoing effort to minimize layer mismatches and improve film performance.

Controlling reagent concentrations and deposition temperatures may be a useful tool to control mismatches and opto-electrical performance of two dimensional materials. Transmittance as a function of resistivity and deposition temperature is shown in Figure 4 (a). Similarly, resistivity as a function of reagent concentration and deposition temperature is shown in Figure 4 (b). The data was interpolated from experimental measurements.

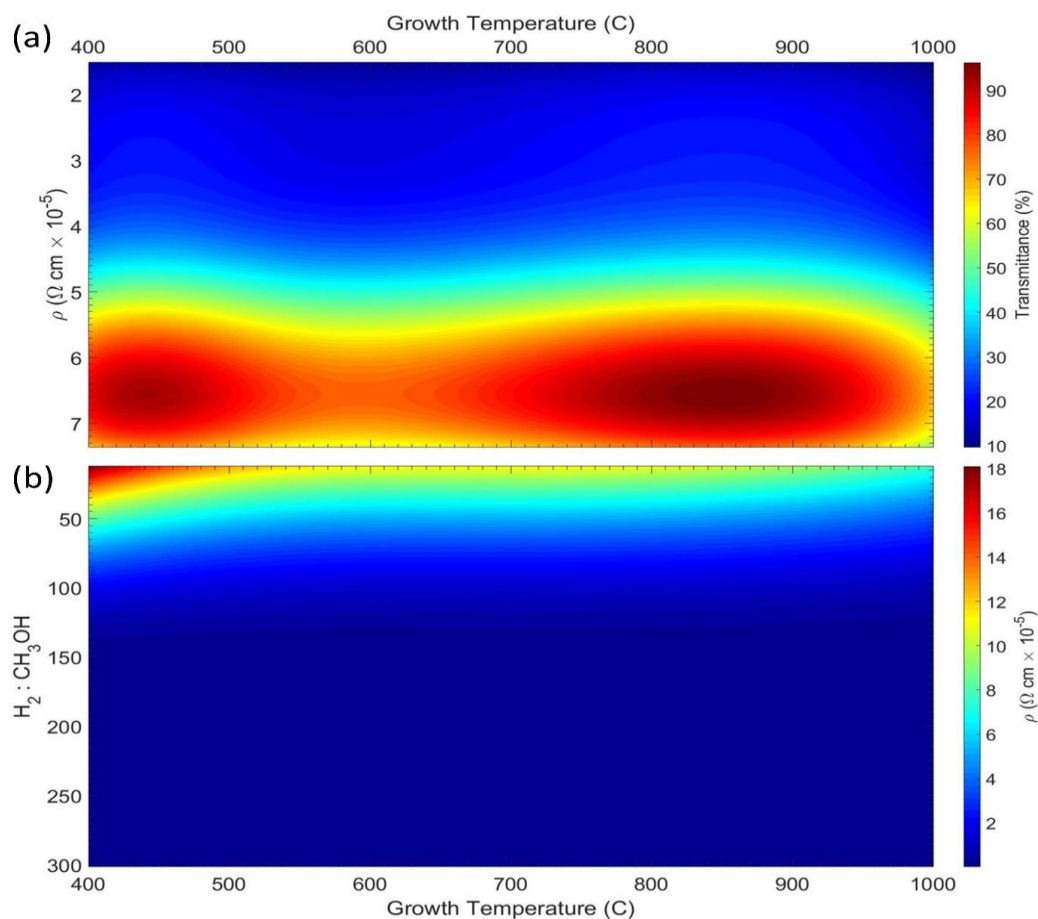


Figure 4. Graphene (a) transmittance as a function of deposition temperature and film resistivity, and (b) resistivity as a function of reagent concentrations and growth temperature in the CVD chamber.

Resistivity decreases at higher temperatures and higher diluent concentrations. This result is expected based upon the above discussion. Higher temperature and lower reagent concentration facilitate a uniform, highly ordered material growth to take place. Highest transmittances are found at the lowest resistivities. The drop in resistivities is attributed to the uniformity achieved at higher deposition temperatures; thus, also facilitating the more favorable optical performance in the films [27] [28].

The experimental results presented demonstrate the power of the chemical vapor deposition method. Film performance can be optimized through a careful consideration of the reagent concentrations, partial pressures, diluent choices, deposition temperatures, and other factors. Thus, highly favorable properties in the thin films can be tuned through proper planning for, and consideration of growth mechanisms.

Despite voluminous experimental data, the growth mechanisms responsible for the film depositions are, as of yet, not fully understood. However, a strong correlation between the opto-electrical performance and the deposition parameters strongly suggests various growth mechanisms present during film growth. More research is required to achieve complete understanding of the CVD and its effect on thin film performance.

CONCLUSION

This work briefly discussed the theoretical and experimental achievements in thin film depositions through chemical vapor deposition. Theoretical derivations suggest it is possible to achieve film growth under a broad combination of deposition parameters. Experimentally, it has been shown that various deposition mechanisms dominate at the various deposition regimes; thus, drastically altering film performance. It is of great interest for academic and commercial parties to define the relationship between film performance and deposition parameters. Although, the initial correlations have been established, much work remains in this field.

It has been shown that film performance can be tuned through temperature and reagent concentrations. Making it possible to achieve desirable film properties through simple experimental manipulations. Furthermore, these techniques are proving to be cost effective and are thus strong candidates for commercial application. It is expected that the current technological limitations will be overcome in the near future, enabling a rise of novel technology for diverse applications.

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REFERENCES

- [1] M. Z. Iqbal, O. Kelekci, M. W. Iqbal and J. Eom, "The structural and electrical evolution of chemical vapor deposition grown graphene by electron beam irradiation induced disorder," *Carbon*, vol. 59, pp. 366-371, 2013.
- [2] A. Slonopas, N. Alijabbari, C. Saltonstall, T. Globus and P. Norris, "Chemically deposited nanocrystalline lead sulfide thin films with tunable properties for use in photovoltaics," *Electrochimica Acta*, vol. 151, pp. 140-149, 2015.
- [3] C. R. Shallcross, J. G. Stanfill and N. R. Armstrong, "Effect of substrate surface free energy on the optoelectronic and morphological properties of organolead halide perovskite solar cell materials," in *Physical Chemistry of Interfaces and Nanomaterials XIV*, San Diego, CA, 2015.
- [4] J. J. Alcantar-Pena, J. Montes, M. J. Arellano-Jimenez, J. E. Ortega-Aguillar, D. Berman-Mendoza, R. Garcia, M. J. Yacaman and O. Auciello, "Low temperature hot filament chemical vapor deposition of Ultrananocrystalline Diamond films with tunable sheet resistance for electronic power devices," *Diamond and Related Materials*, vol. 69, pp. 207-213, 2016.
- [5] A. Slonopas, M. Melia, K. Xie, T. Globus, J. M. Fitz-Gerald and P. Norris, "Factors limiting doping efficiency of Iridium in pulsed laser deposited TiO₂ transparent conducting oxide," *Journal of Material Science*, vol. 51, no. 19, pp. 8995-9004, 2016.
- [6] T. N. Murakami, Y. Kijitori, N. Kawashima and T. Miyasaka, "Low temperature preparation of mesoporous TiO₂ films for efficient dye-sensitized photoelectrode by chemical vapor deposition combined with UV light irradiation," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 164, no. 1-3, pp. 187-191, 2004.
- [7] A. Slonopas, B. J. Foley, J. J. Choi and M. C. Gupta, "Charge transport in bulk CH₃NH₃PbI₃ perovskite," *Journal of Applied Physics*, vol. 119, p. 074101, 2016.
- [8] T. Taima, M. Shahiduzzaman, K. Yamamoto, Y. Furumoto, T. Kuwabara and K. Takahashi, "Planar heterojunction type perovskite solar cells based on TiO_x compact layer fabricated by chemical bath deposition," in *Proceedings SPIE 9749, Oxide-based Materials and Devices VII*, 2016.
- [9] M. M. Tavakoli, L. Gu, Y. Gao, C. Reckmeier, J. He, A. L. Rogach, Y. Yao and Z. Fan, "Fabrication of efficient planar perovskite solar cells using a one-step chemical vapor deposition method," *Scientific Reports*, vol. 5, p. 14083, 2015.
- [10] A. Slonopas, H. Ryan, B. Foley, Z. Sun, K. Sun, T. Globus and P. Norris, "Growth mechanisms and their effects on the opto-electrical properties of CdS

- thin films prepared by chemical bath deposition," *Materials Science in Semiconductor Processing*, vol. 52, pp. 24-31, 2016.
- [11] M. Asif, Y. Tan, L. Pan, J. Li, M. Rashad and M. Usman, "Low temperature hot filament chemical vapor deposition of Ultrananocrystalline Diamond films with tunable sheet resistance for electronic power devices," *The Journal of Physical Chemistry C*, vol. 119, no. 6, pp. 3079-3089, 2015.
- [12] A. L. Thomann, C. Vahlas, L. Aloui, D. Samelot, A. Caillard, N. Shaharil, R. Blanc and E. Millon, "Conformity of Aluminum Thin Films Deposited onto Micro-Patterned Silicon Wafers by Pulsed Laser Deposition, Magnetron Sputtering, and CVD," *Chemical Vapor Deposition*, vol. 17, no. 10-12, pp. 366-374, 2011.
- [13] K. K. Yee, "Protective coatings for metals by chemical vapour deposition," *International Metals Review*, vol. 23, no. 1, pp. 19-42, 2013.
- [14] K. E. Spear, "Principles and applications of chemical vapor deposition (CVD)," *Pure and Applied Chemistry*, vol. 54, no. 7, pp. 1297-1311, 1982.
- [15] R. H. Petrucci, W. S. Harwood, G. E. Herring and J. Madura, *General Chemistry: Principles and Modern Application*, 9th Edition, Newark, NJ: Prentice Hall, 2016.
- [16] Y. Liu, M. Gibbs, J. Puthussery, S. Gaik, R. Ihly, H. W. Hillhouse and M. Law, "Dependence of Carrier Mobility on Nanocrystal Size and Ligand Length in PbSe Nanocrystal Solids," *Nano Letters*, vol. 10, no. 5, pp. 1960-1969, 2010.
- [17] S. Takagi, A. Toriumi and M. Iwase, "On the universality of inversion layer mobility in Si MOSFET's: Part I-effects of substrate impurity concentration," *IEEE Transactions on Electronic Devices*, vol. 41, no. 12, pp. 2357-2362, 1994.
- [18] M. E. Law, M. Lian and D. E. Burk, "Self-consistent model of minority-carrier lifetime, diffusion length, and mobility," *IEEE Electron Device Letters*, vol. 12, no. 8, pp. 401-403, 2002.
- [19] E. Weinan and H. Zhongyi, "Matching Conditions in Atomistic-Continuum Modeling of Materials," *Physical Review Letters*, vol. 87, p. 135501, 2001.
- [20] A. Stukowski, "Computational Analysis Methods in Atomistic Modeling of Crystals," *The Journal of The Minerals, Metals & Materials Society (TMS)*, vol. 66, no. 3, pp. 399-407, 2014.
- [21] V. Melnikova, "The Cluster Growth Mechanism of Nanostructured Diamond," in *Hydrogen Materials Science and Chemistry of Carbon Nanomaterials*, Springer, 2007, pp. 557-562.
- [22] K. S. Novoselov, A. 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*, vol. 306, no. 5696, pp. 666-669, 2004.

- [23] S. Bhaviripudi, X. Jia, M. L. Dresselhaus and J. Kong, "Role of Kinetic Factors in Chemical Vapor Deposition Synthesis of Uniform Large Area Graphene Using Copper Catalyst," *Nano Letters*, vol. 10, pp. 4128-4133, 2010.
- [24] I. Pocsik, M. Hundhausen, M. Koos and L. Ley, "Origin of the D peak in the Raman spectrum of microcrystalline graphite," *Journal of Non-Crystalline Solids*, Vols. 227-230, pp. 1083-1086, 1998.
- [25] F. Tuinstra and J. L. Koenig, "Raman Spectrum of Graphite," *The Journal of Chemical Physics*, vol. 53, p. 1126, 1970.
- [26] A. C. Ferrari and J. Robertson, "Interpretation of Raman spectra of disordered and amorphous carbon," *Physical Review B*, vol. 61, no. 20, p. 14095, 1999.
- [27] J. Chan, A. Venugopal, A. Pirkle, S. McDonnell, D. Hinojos, C. W. Magnuson, R. S. Ruoff, L. Colombo, R. M. Wallace and E. m. Vogel, "Reducing Extrinsic Performance-Limiting Factors in Graphene Grown by Chemical Vapor Deposition," *ACS Nano*, vol. 6, no. 4, pp. 3224-3229, 2012.
- [28] W. Liu, H. Li, C. Xu, Y. Khatami and K. Banerjee, "Synthesis of high-quality monolayer and bilayer graphene on copper using chemical vapor deposition," *Carbon*, vol. 49, no. 13, pp. 4122-4130, 2011.