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Editorial

Recent Advances in Graphene Epitaxial Growth: Aspects of Substrate Surface Modification Using Coatings

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Since the discovery of graphene in 2004 [1], it has attracted enormous interest in various fields of industry, university, and research institutes studying electronics, physics, chemistry, and engineering fields on account of its potential in high-tech applications. A huge number of papers have been published on graphene, and there has been significant news coverage in many journals and in the mass media. This manuscript introduces the epitaxial-growing graphene and its recent use in high-tech applications. Despite having already published many application papers on this topic, we remain focused on obtaining new information about developments in high technologies [utilizing unique graphene sheets and finally on their application in real, valuable products.

Graphene is an allotropic modification of the hexagonal structure of single-layer carbon bonded by sp^2 bonds. In addition to being used in electronic components, solar cells, displays, supercapacitors, and various sensors, the use of graphene as a hardening [2], anticorrosive coating is also of interest [3]. The use of graphene as a conductive coating is also promising in the field of flexible electronics [4]. There is growing interest in the use of graphene in the area of charge-and-spin transport, which is promising for the field of spintronic devices [5]. Thus, we can say that graphene is promising in almost all areas of industry, ranging from aerospace to consumer electronics.

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Somewhat surprisingly, with so many applications for graphene, the question remains as to why many products have yet to hit the market. In fact, the answer is obvious: the economical production of industrial graphene has not yet been developed; moreover, each area of application has its own technological difficulties in obtaining graphene. Epitaxial graphene (EG) is obtained by various methods: thermal distortion, high-temperature sublimation, vapor-phase epitaxy, plasma deposition, physical transport, and others. In these methods, one obvious feature is noticed which makes it difficult to implement this technology and scale it up in industry: the quality of the resulting graphene layers and the domain sizes are not high enough. Thus, it is necessary to comprehensively focus on the growth mechanisms and properties of graphene on the surface of the substrate, and the development of the design of heterostructures. If we consider this from the point of view of the uniqueness of the properties of graphene, then initially, the research interest was focused on one atomic layer. Next, researchers began studying two-layer graphene, which showed its amazing transport properties in a combination of two layers, and then three layers [6]. Two-layer graphene showed unique properties when two layers were displaced by a certain angle θ relative to each other by the so-called "magic angle". The properties of van der Waals materials generally differ greatly depending on the order of the atoms between the layers, but this order is difficult to control. Three-layer graphene is placed either in a semi-metallic configuration or in a semiconductor configuration with a controlled band gap.

It is known that graphene mono- and multilayers grow on SiC crystals at high temperatures in an ultrahigh vacuum. The properties of the graphene layer also differ depending on the orientation of the substrate surface to the top (Si or C faces) [7–10], pretreatment [11]. Twisted two-layer graphene can be grown on the C-face. In contrast to graphite, charge carriers in graphene exhibit the properties of Dirac particles (i.e., weak antilocalization and field dependence of the square root of the Landau level energies, an anomalous Berry phase). EG exhibits quasi-ballistic transfer and long coherence length, properties that can be maintained at temperatures above cryogenic levels [12]. It has been shown that graphene multilayers grown on the C-face using the controlled sublimation method consist of unbonded graphene layers with high mobility [13]. Roughening the surface will result in an almost free separation of the epitaxial graphene from the SiC substrate, which exhibits a property close to free [14]. In this work, there was a sharp increase in the I_{2D}/I_G ratio and a redshift in the 2D band in the Raman spectrum, and the compressive stress in the epitaxial graphene layer was reduced by 63%. To achieve high quality and domain sizes, the thermal distortion method has been modernized [15]. The paper called the method "face-to-face".

One of the methods for separating graphene sheets from a substrate is hydrogen intercalation, which creates quasi-free layers on the SiC (0001) surface [16]. The quantum Hall resistance is consistent with the nominal value (half of the Klitzing background constant) within a standard deviation of 4.5×10^{-9}, which makes this method suitable for the manufacture of electrical quantum standards. The crystallinity of epitaxial graphene grown on 6H-SiC is also improved by using a buffer layer coated with metals, for example Mo [17]. The Mo layer causes the accumulation of heat on the surface of the substrate, due to the reflection of thermal radiation, and increases the partial pressure of silicon near the surface by retaining sublimated silicon atoms between the substrate and the metal. In parallel, methods are being developed for carrying graphene on cost-effective 3C-SiC/Si heterosubstrates [18,19].

The nucleation of the graphene layer is also stimulated by means of catalysts [20]. By selectively oxidizing the reverse side of the copper foil before growing graphene, a sharp decrease in the graphene nucleation density by six orders of magnitude is achieved. The role of pinning points in epitaxial graphene moiré superstructures on a Pt(111) surface is also considered [21]. These points are responsible for the development of the superstructure, while the charge from the Pt substrate is injected into graphene, causing local n doping, mainly localized at these specific positions of the anchoring points.

It was noted above that two-layer graphene with a relative twist of layers is also of interest. As a rule, the electrical conductivity will increase monotonically with a decrease in the angle of twist, due to increased bonding between adjacent layers [22]. Highly homogeneous two-layer graphene was obtained on an epitaxial Cu–Ni(111) alloy [23]. It is found that the relative concentration of Ni and Cu, as well as the growth temperature and cooling profile, strongly affect the uniformity of graphene layers. Metastable orientations with a rotation of 30° were also observed in both the upper and lower layers. An anomalous conductivity arises in two-layer graphene twisted at a small angle. Large domains with arbitrary twist angles are obtained with an accuracy of <1.0° [24]. There are many theoretical papers on models covering global effects, such as proximity to substrates, and local spin–orbit coupling (SOC) effects arising, for example, from the functionalization of a dilute adsorbant [25]. The densities of states of a graphene monolayer interacting with the SiC surface are calculated [26]. It is shown that the interaction of graphene with a substrate leads to a narrow gap ~$0.01 \div 0.06$ eV in the graphene density of states. A simulation of complex longitudinal low-frequency conduction was carried out with an emphasis on the effects of spatial dispersion. A spatial periodic polarization is proposed in graphene models with pseudo-Majorana charge carriers [27]. In twisted monolayer–two-layer graphene, electrically tuned correlated and topological states have been revealed. Graphene also exhibits interesting quantum effects with other two-dimensional materials. For example, the effect of proximity in graphene was studied on monolayers of phosphorus trichalcogenides of transition metals [28]. It has been shown that the influence of SOC on the maximized Dirac variance is negligibly small compared to the exchange coupling.

When doping Ca with certain atoms, graphene also exhibits superconducting properties [29]. The paper reports reliable superconductivity in all Ca-doped graphene laminates. They become superconducting at temperatures (T_c) 4–6 K, while T_c depends strongly on the localization of the Ca layer and the concentration of induced charge carriers in graphene. In three-layer graphene, superconductivity tunable by an electric field with a variable rotation at a magic angle was also observed [30]. A mechanism of reliable superconductivity of the Bardeen–Cooper–Schrieffer type in graphene placed near a Bose–Einstein condensation is proposed [31]. New physical properties in such systems, such as unconventional superconductivity, arise from the dispersionless flat band that appears when the twist reaches a magic angle [32].

The development of spintronic devices is based on the efficient generation of spin-polarized currents and their control, with the help of an electric field [33]. It has recently been reported that graphene grown on Ni(111) exhibits a Rashba effect that depends on magnetization [34]. In graphene, manifestations of 1D properties that differ from 2D is possible [35]. The transport properties of epitaxial graphene on SiC (0001) in quantizing magnetic fields are investigated [36]. The paper shows that the transport properties in the quantum Hall regime are strongly affected by the presence of inclusions of two layers, and a significant deviation from the usual quantum Hall characteristics was observed. A quantitative model of enhanced interchannel scattering due to the presence of two-layer inclusions is presented, which successfully explains the observed symmetry properties. [37]. In graphene superlattices near the primary Dirac point, the topological currents of the valley are determined through ballistic edge modes [38]. This will make it possible to electrically rebuild ferromagnetism when the conduction band is filled by a quarter and the associated anomalous Hall effect.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric field in atomically thin carbon films. *Science* **2004**, *306*, 666–669. [CrossRef] [PubMed]
2. Van Hau, T.; Van Trinh, P.; Hoai Nam, N.P.; Van Tu, N.; Lam, V.D.; Phuong, D.D.; Minh, P.N.; Thang, B.H. Electrodeposited nickel-graphene nanocomposite coating: Effect of graphene nanoplatelet size on its microstructure and hardness. *RSC Adv.* **2020**, *10*, 22080–22090. [CrossRef] [PubMed]
3. Cui, G.; Bi, Z.; Zhang, R.; Liu, J.; Yu, X.; Li, Z. A comprehensive review on graphene-based anti-corrosive coatings. *Chem. Eng. J.* **2019**, *373*, 104–121. [CrossRef]
4. Yu, J.; Wang, L.; Hao, Z.; Luo, Y.; Sun, C.; Wang, J.; Han, Y.; Xiong, B.; Li, H. Van der Waals Epitaxy of III-Nitride Semiconductors Based on 2D Materials for Flexible Applications. *Adv. Mater.* **2020**, *32*, 1903407. [CrossRef] [PubMed]
5. Phillips, M.; Mele, E.J. Charge and spin transport on graphene grain boundaries in a quantizing magnetic field. *Phys. Rev. B* **2017**, *96*, 041403. [CrossRef]
6. Gao, Z.; Wang, S.; Berry, J.; Zhang, Q.; Gebhardt, J.; Parkin, W.M.; Avila, J.; Yi, H.; Chen, C.; Hurtado-Parra, S.; et al. Large-area epitaxial growth of curvature-stabilized ABC trilayer graphene. *Nat. Commun.* **2020**, *11*, 546. [CrossRef]
7. Yazdi, G.; Iakimov, T.; Yakimova, R. Epitaxial Graphene on SiC: A Review of Growth and Characterization. *Crystals* **2016**, *6*, 53. [CrossRef]
8. Kruskopf, M.; Pierz, K.; Wundrack, S.; Stosch, R.; Dziomba, T.; Kalmbach, C.C.; Müller, A.; Baringhaus, J.; Tegenkamp, C.; Ahlers, F.J.; et al. Epitaxial graphene on SiC: Modification of structural and electron transport properties by substrate pretreatment. *J. Phys. Condens. Matter* **2015**, *27*, 185303. [CrossRef]
9. Norimatsu, W.; Kusunoki, M. Epitaxial graphene on SiC{0001}: Advances and perspectives. *Phys. Chem. Chem. Phys.* **2014**, *16*, 3501–3511. [CrossRef]
10. Briggs, N.; Gebeyehu, Z.M.; Vera, A.; Zhao, T.; Wang, K.; De La Fuente Duran, A.; Bersch, B.; Bowen, T.; Knappenberger, K.L.; Robinson, J.A. Epitaxial graphene/silicon carbide intercalation: A minireview on graphene modulation and unique 2D materials. *Nanoscale* **2019**, *11*, 15440–15447. [CrossRef]
11. Chatterjee, A.; Kruskopf, M.; Wundrack, S.; Hinze, P.; Pierz, K.; Stosch, R.; Scherer, H. Impact of Polymer-Assisted Epitaxial Graphene Growth on Various Types of SiC Substrates. *ACS Appl. Electron. Mater.* **2022**, *4*, 5317–5325. [CrossRef]
12. de Heer, W.A.; Berger, C.; Wu, X.; First, P.N.; Conrad, E.H.; Li, X.; Li, T.; Sprinkle, M.; Hass, J.; Sadowski, M.L.; et al. Epitaxial graphene. *Solid State Commun.* **2007**, *143*, 92–100. [CrossRef]
13. De Heer, W.A.; Berger, C.; Ruan, M.; Sprinkle, M.; Li, X.; Hu, Y.; Zhang, B.; Hankinson, J.; Conrad, E. Large area and structured epitaxial graphene produced by confinement controlled sublimation of silicon carbide. *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 16900–16905. [CrossRef] [PubMed]
14. Hu, T.; Bao, H.; Liu, S.; Liu, X.; Ma, D.; Ma, F.; Xu, K. Near-free-standing epitaxial graphene on rough SiC substrate by flash annealing at high temperature. *Carbon N. Y.* **2017**, *120*, 219–225. [CrossRef]

15. Yu, X.Z.; Hwang, C.G.; Jozwiak, C.M.; Köhl, A.; Schmid, A.K.; Lanzara, A. New synthesis method for the growth of epitaxial graphene. *J. Electron. Spectros. Relat. Phenom.* **2011**, *184*, 100–106. [CrossRef]
16. Szary, M.J.; El-Ahmar, S.; Ciuk, T. The impact of partial H intercalation on the quasi-free-standing properties of graphene on SiC(0001). *Appl. Surf. Sci.* **2021**, *541*, 148668. [CrossRef]
17. Jin, H.B.; Jeon, Y.; Jung, S.; Modepalli, V.; Kang, H.S.; Lee, B.C.; Ko, J.H.; Shin, H.J.; Yoo, J.W.; Kim, S.Y.; et al. Enhanced Crystallinity of Epitaxial Graphene Grown on Hexagonal SiC Surface with Molybdenum Plate Capping. *Sci. Rep.* **2015**, *5*, 9615. [CrossRef]
18. Suemitsu, M.; Jiao, S.; Fukidome, H.; Tateno, Y.; Makabe, I.; Nakabayashi, T. Epitaxial graphene formation on 3C-SiC/Si thin films. *J. Phys. D Appl. Phys.* **2014**, *47*, 094016. [CrossRef]
19. Ramazanov, S.M.; Ramazanov, G.M. Relaxing layers of silicon carbide grown on a silicon substrate by magnetron sputtering. *Technical Phys. Lett.* **2014**, *40*, 44–47. [CrossRef]
20. Braeuninger-Weimer, P.; Brennan, B.; Pollard, A.J.; Hofmann, S. Understanding and Controlling Cu-Catalyzed Graphene Nucleation: The Role of Impurities, Roughness, and Oxygen Scavenging. *Chem. Mater.* **2016**, *28*, 8905–8915. [CrossRef]
21. Martínez, J.I.; Merino, P.; Pinardi, A.L.; Gonzalo, O.I.; López, M.F.; Méndez, J.; Martín-Gago, J.A. Role of the Pinning Points in epitaxial Graphene Moiré Superstructures on the Pt(111) Surface. *Sci. Rep.* **2016**, *6*, 20354. [CrossRef]
22. Zhang, S.; Song, A.; Chen, L.; Jiang, C.; Chen, C.; Gao, L.; Hou, Y.; Liu, L.; Ma, T.; Wang, H.; et al. Abnormal conductivity in low-angle twisted bilayer graphene. *Sci. Adv.* **2020**, *6*, abc5555. [CrossRef] [PubMed]
23. Takesaki, Y.; Kawahara, K.; Hibino, H.; Okada, S.; Tsuji, M.; Ago, H. Highly Uniform Bilayer Graphene on Epitaxial Cu-Ni(111) Alloy. *Chem. Mater.* **2016**, *28*, 4583–4592. [CrossRef]
24. Liu, C.; Li, Z.; Qiao, R.; Wang, Q.; Zhang, Z.; Liu, F.; Zhou, Z.; Shang, N.; Fang, H.; Wang, M.; et al. Designed growth of large bilayer graphene with arbitrary twist angles. *Nat. Mater.* **2022**, *21*, 1263–1268. [CrossRef] [PubMed]
25. Kochan, D.; Irmer, S.; Fabian, J. Model spin-orbit coupling Hamiltonians for graphene systems. *Phys. Rev. B* **2017**, *95*, 165415. [CrossRef]
26. Davydov, S.Y. Electronic states in epitaxial graphene fabricated on silicon carbide. *Semiconductors* **2011**, *45*, 1070–1076. [CrossRef]
27. Chen, S.; He, M.; Zhang, Y.H.; Hsieh, V.; Fei, Z.; Watanabe, K.; Taniguchi, T.; Cobden, D.H.; Xu, X.; Dean, C.R.; et al. Electrically tunable correlated and topological states in twisted monolayer–bilayer graphene. *Nat. Phys.* **2021**, *17*, 374–380. [CrossRef]
28. Zollner, K.; Fabian, J. Proximity effects in graphene on monolayers of transition-metal phosphorus trichalcogenides M PX3 (M:Mn, Fe, Ni, Co, and X: S, Se). *Phys. Rev. B* **2022**, *106*, 035137. [CrossRef]
29. Chapman, J.; Su, Y.; Howard, C.A.; Kundys, D.; Grigorenko, A.N.; Guinea, F.; Geim, A.K.; Grigorieva, I.V.; Nair, R.R. Superconductivity in Ca-doped graphene laminates. *Sci. Rep.* **2016**, *6*, 23254. [CrossRef] [PubMed]
30. Hao, Z.; Zimmerman, A.M.; Ledwith, P.; Khalaf, E.; Najafabadi, D.H.; Watanabe, K.; Taniguchi, T.; Vishwanath, A.; Kim, P. Electric field–tunable superconductivity in alternating-twist magic-angle trilayer graphene. *Science* **2021**, *371*, 1133–1138. [CrossRef]
31. Sun, M.; Parafilo, A.V.; Villegas, K.H.A.; Kovalev, V.M.; Savenko, I.G. Bose–Einstein condensate-mediated superconductivity in graphene. *2D Mater.* **2021**, *8*, 031004. [CrossRef]
32. Wu, D.; Pan, Y.; Min, T. Twistronics in Graphene, from Transfer Assembly to Epitaxy. *Appl. Sci.* **2020**, *10*, 4690. [CrossRef]
33. Avsar, A.; Tan, J.Y.; Taychatanapat, T.; Balakrishnan, J.; Koon, G.K.W.; Yeo, Y.; Lahiri, J.; Carvalho, A.; Rodin, A.S.; O'Farrell, E.C.T.; et al. Spin–orbit proximity effect in graphene. *Nat. Commun.* **2014**, *5*, 4875. [CrossRef] [PubMed]
34. Rader, O.; Varykhalov, A.; Sánchez-Barriga, J.; Marchenko, D.; Rybkin, A.; Shikin, A.M. Is there a Rashba effect in graphene on 3d ferromagnets? *Phys. Rev. Lett.* **2009**, *102*, 057602. [CrossRef]
35. Karakachian, H.; Nguyen, T.T.N.; Aprojanz, J.; Zakharov, A.A.; Yakimova, R.; Rosenzweig, P.; Polley, C.M.; Balasubramanian, T.; Tegenkamp, C.; Power, S.R.; et al. One-dimensional confinement and width-dependent bandgap formation in epitaxial graphene nanoribbons. *Nat. Commun.* **2020**, *11*, 6380. [CrossRef]
36. Iagallo, A.; Tanabe, S.; Roddaro, S.; Takamura, M.; Sekine, Y.; Hibino, H.; Miseikis, V.; Coletti, C.; Piazza, V.; Beltram, F.; et al. Bilayer-induced asymmetric quantum Hall effect in epitaxial graphene. *Semicond. Sci. Technol.* **2015**, *30*, 055007. [CrossRef]
37. Rutter, G.M.; Crain, J.N.; Guisinger, N.P.; Li, T.; First, P.N.; Stroscio, J.A. Scattering and Interference in Epitaxial Graphene. *Science* **2007**, *317*, 219–222. [CrossRef]
38. Li, Y.; Amado, M.; Hyart, T.; Mazur, G.P.; Robinson, J.W.A. Topological valley currents via ballistic edge modes in graphene superlattices near the primary Dirac point. *Commun. Phys.* **2020**, *3*, 224. [CrossRef]