

High-Yield Etching-Free Transfer of Graphene: A Fracture Mechanics Approach

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Abstract: Transfer is the critical issue of producing high-quality and scalable graphene electronic devices. However, conventional transfer processes require the removal of an underlying metal layer by wet etching process, which induces significant economic and environmental problems. We propose the etching-free mechanical releasing of graphene using polymer adhesives. A fracture mechanics approach was introduced to understand the releasing mechanism and ensure high-yield process. It is shown that the thickness of adhesive and target substrate affect the transferability of graphene. Based on experimental and fracture mechanics simulation results, we further observed that compliant adhesives can reduce the adhesive stress during the transfer, which also enhances the success probability of graphene transfer.

Keywords: Graphene, Transfer, Etching-Free, Fracture

1. Introduction

For the past decade, graphene has successfully showed possibility beyond existing physical limitations.¹⁻⁵⁾ Significant research has been directed to the development of graphene for the applications such as transparent electrodes, transistors, and also encapsulation layers for microelectronics packaging. The development of chemical vapor deposition (CVD) process enables the synthesis of large-area and high-quality graphene⁶⁻⁸⁾, which has been applied in various fields.^{5,9,10)} However, after the growth the graphene should be separated from the underneath metal and transferred to another surface such as a dielectric or organic layer.^{2,11-13)} Therefore, the development of a reliable transfer process is critical for the successful fabrication of graphene devices.

The general transfer process of synthesized graphene relies on the removal of the underlying metal layer, and graphene should be held simultaneously with a sacrificial organic layer.^{2,8,14-17)} The transfer methods can be applicable to roll-to-roll processes¹⁸⁾ and to flexible substrates.¹⁹⁾ Even though it is scalable and adaptable to any substrate, there are still serious problems to be solved. The metal etching process is not economical for the mass production because the metal substrate is not reusable, and wet process can cause wrinkles and defects on graphene. Additionally, removing sacrificial layer is also challenging, and the

resulting polymer residues degrade the electrical conductivity of graphene.

Recent research showed that etching-free graphene transfer is an alternative to overcoming these disadvantages of etching based graphene transfer. The etching-free graphene transfer process is based on the delamination of graphene from metal substrates, and there are two ways. One is an electrochemical delamination.^{20,21)} Electrochemical reactions produce hydrogen bubbles at cathode which induce delamination on graphene/metal interfaces. However, the methods still involve a wet process and a sacrificial layer should be removed also. Another route for the etching-free transfer is mechanical delamination.²²⁻²⁴⁾ A polymer layer is adhered to the graphene surface with higher adhesion than that of graphene-metal, and then mechanical loading is applied to induce fracture at the graphene/metal interface. Although graphene should be adhered to the polymer surface, the transfer is an entirely dry process.

The mechanical delamination-based graphene transfer is an entirely dry process, and is therefore well compatible with efficient mass production. Although, the polymer residue is unavoidable due to an epoxy, the transfer can be directly used in specific applications such as transparent electrodes and organic electronics. In order to ensure high-yield transfer, strong bonding at the adhesive/graphene interface is required and various mechanical conditions should be

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optimized to induce stable crack propagation. From the point of crack propagation, the dimensions and mechanical properties of the metal substrate, the adhesive and target substrate become critical for precisely guiding the crack at graphene/metal interfaces.²⁵⁻²⁷⁾ Although these mechanical conditions are expected to dominate the transferability of graphene, it has not been systematically researched yet.

Here, we show the etching-free transfer of graphene using mechanical release. We investigated its release mechanics and propose a guideline for the high-yield mechanical transfer of graphene. The release of graphene was characterized with Raman spectroscopy, which showed that graphene release is strongly dependent on the thickness of the target substrate and adhesive. Finally, it is shown that the mechanical properties of the adhesive, such as Young's modulus and hardness, affect transfer yield, which is also confirmed by fracture mechanics simulation.

2. Experimental

Synthesized monolayer graphene on a 27- μm thick Cu sheet by CVD process was used. As shown in Fig. 1a and 1b, the topography of the graphene on Cu was captured by an optical surface profiler. The image shows striations on the surface, which is induced by rolling process of Cu sheet. The measured RMS roughness of the Cu sheet was 314 nm. The surface is rougher than other thin metal films grown on silicon wafers. Using the synthesized graphene on Cu sheet, we tried etching-free transfer. The basic process is shown in Fig. 1c. Epoxy adhesive is applied on the graphene surface, and target substrate is covered. After the thermal curing of the adhesive, mechanical bending was applied to delaminate the graphene from Cu sheet.

3. Results and Discussion

To ensure graphene transfer, the adhesion of graphene/adhesive interface should be higher than that of graphene/metal interface. It is already reported that graphene adhesion is based on weak van der Waals force, and the adhesion energy of graphene on metal is slightly higher than that on dielectric.^{24,28)} Nevertheless, the energy level of physical bonding is significantly lower than that of chemical bonding, so that graphene/adhesive adhesion is strong enough to hold the graphene during the mechanical releasing. Moreover, the fracture mechanics should be considered for the stable crack propagation at the graphene/metal interface.

The thickness effects of adhesive and target substrate were investigated. The graphene transfer process is based on

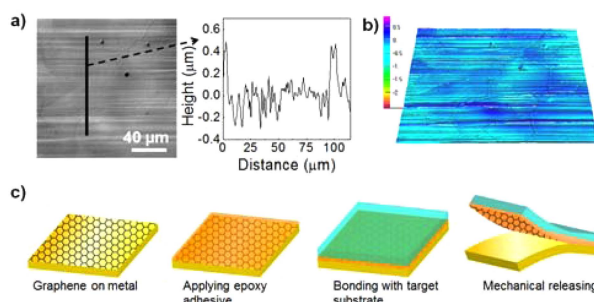


Fig. 1. Topography of (a) the Cu surface, and (b) its three-dimensional image. (c) Schematic illustration of the etching-free graphene transfer process.

a mechanical fracture of heterogeneous interface, and the thickness becomes crucial to induce stable crack propagation at the graphene/metal interface. The epoxy adhesives with different thicknesses of 2 μm and 30 μm were used and 50 μm and 190 μm thick target PET substrates were selected.

Capillary force of a liquid adhesive and thermo-compression bonding enabled very thin adhesive coating between target and metal substrates. The thick adhesive

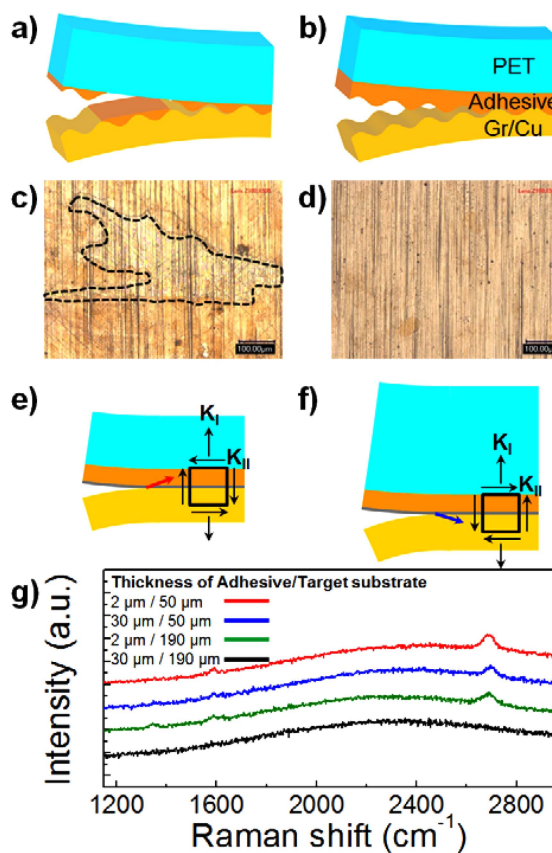


Fig. 2. Debond morphology of (a) thin, and (b) thick adhesives. Optical image on the Cu surface after the transfer of (c) thin, and (d) thick adhesives. Mixed-mode crack deflection of (e) thin, and (f) thick target substrates. (g) Raman spectra on the Cu surface after the transfer.

sample was fabricated by Teflon sheet having the same thickness. The schematics of fabricated specimens were shown in Fig. 2a and 2b. The thin adhesive sample shows epoxy residue on metal due to the rough morphology of Cu sheet. The thickness of epoxy is 2 μm , and it is comparable to the peak-to-valley height of the metal striations. These wavy patterns on metal are imprinted on epoxy adhesive, and therefore the epoxy thickness is varied across the striations.

It is known that irregular shape makes stress concentration, hence the stress is concentrated on the thinner adhesive region. The locally concentrated stress causes the fracture of the epoxy layer, and it leaves epoxy residue on graphene/metal surfaces, which is also confirmed by optical image as shown in Fig. 2c. To address the residue issue, thick adhesive was investigated. After the mechanical releasing with the thick adhesive, the Fig. 2d shows clean and smooth surface on metal sheet.

The thickness of target substrate is also a critical factor for the mechanical delamination. It determines the crack deflection on heterogeneous interfaces. In the case of symmetric substrate having the same thickness and Young's modulus, the crack can propagate straight.²⁹⁾ However, the thickness and Young's modulus of each layer are different from each other. To induce the stable crack propagation on the graphene/metal interface, the crack should be straight. If not, the crack should deflect into the graphene/metal substrate.

Even though the crack deflects into metals, high toughness of the metal sheets prevents the crack kinking. The worst situation is the crack deflection into the target substrate. In this situation, adhesive layer can be easily fractured because of its brittleness. The deflection angle of the crack is determined by two factors: Young's modulus and thickness of the interfacing materials.^{25,26)} The rule of thumb for determining crack kink direction is that the crack deflects into a compliant substrate. We used thin (50 μm) and thick (190 μm) target substrates. The 50 μm PET layer has lower bending stiffness than that of Cu layer, therefore the crack will deflect on a target substrate which is shown in Fig. 2e. It is obvious that the thicker substrate is stiffer, so that the direction of crack kinking is changed to the graphene/metal (Fig. 2f).

To verify the hypothesis, four specimens were fabricated with different thickness of adhesive and target-substrate. Raman spectroscopy was used to characterize the fractured surface of metal, which gives the exact information of the actual crack path. The three independent spots were selected on each sample for the acquisition of Raman spectra. As

shown in Fig. 2g, the thick-thick specimen shows no graphene peak on metal while the other specimens have graphene peaks at 2700 cm^{-1} and 1690 cm^{-1} .³⁰⁾ It can be explained that the thick-thick specimens is the only viable conditions for the mechanical release of graphene. In other words, the success of graphene transfer is highly dominated by thickness of interfacial layers. The sheet resistances of the dry-transferred and wet-transferred graphene were compared by four-point-probe, which were 8,338 \pm 1,841 Ω/\square and 1,038 \pm 180 Ω/\square , respectively. The low electrical conductivity of dry-transferred graphene can be tuned by chemical doping, and further study is required to control the quality of dry-transferred graphene.

It was mentioned that the local stress-concentration causes the fracture of epoxy layer. To deal with this issue, we used three kinds of commercial epoxy adhesive (353nd, 301 and 305, EPO-TEK[®], USA), and performed same experiment at each thickness condition. The results are marked in Table 1. The transferability was characterized by Raman spectrum on Cu and electrical resistance measurement on target substrate. As seen in previous results, the 353nd has poor transferability, only success in thick-thick condition. However, the 301 shows better transferability; thick-adhesive enabled the transfer. It can be interpreted by the residue problem. The thick adhesive prevents local stress-concentration on epoxy layer, which does not leave any residue on metal. In contrast, the 305 adhesive showed one hundred percent of transferability. At the thick-thick condition, every adhesive is a good candidate for the graphene transfer. Each adhesive has a potential to delaminate the graphene from metal with good adhesion, however some adhesives, such as 353nd and 301, are sensitive to the dimensions of interfacial layers. The difference can be attributed to the mechanical properties of each adhesive. Shore D hardness and Young's modulus of each adhesive are plotted in Fig. 3.

There is a connection between these properties and transferability. Hardness is a measure of how the material resist to permanent change, which is also represent the brittleness of the material. The lower hardness material can

Table 1. The transferability of graphene with different dimensions and adhesives.

Adhesive thickness	Target substrate thickness	EPO-TEK [®] 353nd	EPO-TEK [®] 301	EPO-TEK [®] 305
2 μm	50 μm	×	×	○
30 μm	50 μm	×	○	○
2 μm	190 μm	×	×	○
30 μm	190 μm	○	○	○

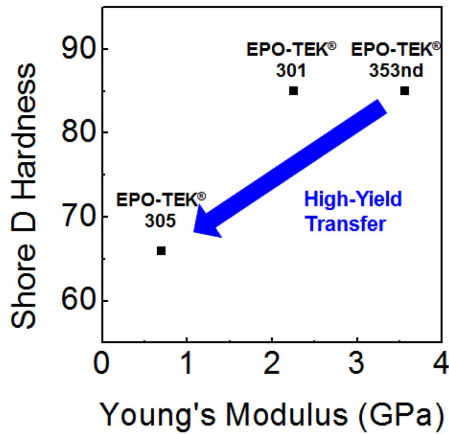


Fig. 3. Young's modulus and hardness of each adhesive.

sustain the more mechanical loading and deformation without fracture. Young's modulus is the intrinsic property of materials, and relates the deformation to load. It is expected that the lower Young's modulus yields the lower mechanical stress at the same transfer condition. However, it is not the simple in mechanical fracture. The fracture energy should be considered to compare the stress in different adhesives.

To evaluate the effect of Young's modulus on the stress of adhesives, we simulated the mechanical fracture. The commercial tool, ABAQUS, was used, and linear-elastic behavior was assumed.

Dimensions and Young's modulus of each specimen condition was inputted, therefore total twelve conditions were simulated. The upper part of the specimen (Fig. 4a), adhesive and target substrate, was modeled and the other part was assumed to be rigid by fixed boundary conditions. Global mesh size and crack-tip mesh size were $2\ \mu\text{m}$ and $0.2\ \mu\text{m}$, respectively. The basic assumption for the simulation is that fracture energy is same at each condition. Based on the previous research²⁴⁾, we assumed that the fracture energy of graphene/copper interface is constantly $0.72\ \text{Jm}^{-2}$. Then, the exact peeling load can be determined by matching J-integral value with the fracture energy. After assigning the exact load value, each modeling can be compared under the same fracture status. The von mises stress was probed at the $5\ \mu\text{m}$ in front of the crack tip, because the crack-tip stress value has high singularity.

As mentioned earlier, the thickness and mechanical properties of adhesive and target substrate dominate the transferability of graphene. The results can be quantitatively analyzed by stress calculation, as shown in Fig. 4c. It appears that the low modulus adhesive shows low stress level at crack-tip. Moreover, the stress was reduced with

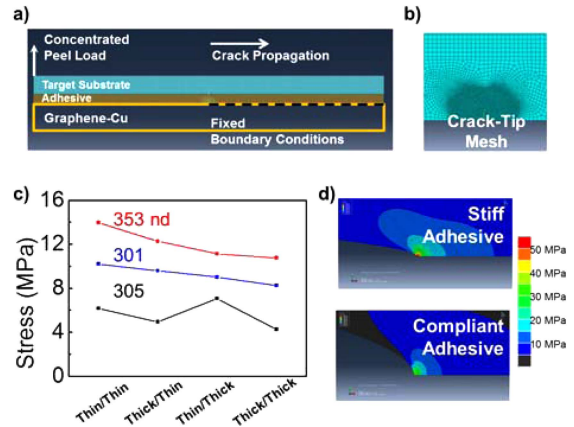


Fig. 4. (a) Boundary and loading conditions of fracture simulation. (b) Crack-tip mesh of the modeling. (c) Stress plot of each specimen. (d) Stress field comparison between stiff and compliant adhesives.

increasing thickness of adhesive and target substrate. As shown in Fig. 4d, the stiff adhesive shows the high level of stress at the crack tip that can induce fracture of adhesive film. Even though the deformation is more severe in the compliant adhesive, the stress is low due to the low Young's modulus. As a result, a compliant adhesive is favorable to graphene transfer, in terms of preventing fracture of adhesive.

4. Conclusions

In conclusion, we proposed the design rule of mechanical releasing of graphene. We found that thin adhesives cause the local stress concentration in the adhesive, which lowers the transferability of graphene by fracture of the adhesive. Moreover, thin target substrates induce crack deflection onto the adhesive layer, which is also unfavorable to the graphene transfer. The mechanical properties of adhesive were considered by experimental results and fracture mechanics simulation. It was found that compliant adhesives reduce the exerted stress on the adhesive, and therefore graphene can be successfully transferred without fracture of the adhesive. We believe that these results can be used for the design criteria of etching-free transfer, and provide a new opportunity for the commercialization of large-area and high-quality graphene electronic devices.

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References

1. A. K. Geim and K. S. Novoselov, "The rise of graphene", *Nature Materials.*, 6(3), 183 (2007).
2. S. K. Bae, H. K. Kim, Y. B. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Özyilmaz, J.-H. Ahn, B. H. Hong and S. Iijima, "Roll-to-roll production of 30-inch graphene films for transparent electrodes", *Nature Nanotechnology.*, 5, 574 (2010).
3. J. S. Bunch, A. M. van der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead and P. L. McEue, "Electromechanical Resonators from Graphene Sheets", *Science.*, 315(5811), 490 (2007).
4. S. S. Roy and M. S. Arnold, "Improving Graphene Diffusion Barriers via Stacking Multiple Layers and Grain Size Engineering", *Advanced Functional Materials.*, 23(29), 3638 (2013).
5. F. Schwierz, "Graphene transistors", *Nature nanotechnology* 5(7), 487 (2010).
6. A. Reina, X. Jia, J. Ho, D. Nezich, H. B. Son, V. Bulovic, M. S. Dresselhaus and J. Kong, "Large Area, Few-Layer Graphene Films on Arbitrary Substrates by Chemical Vapor Deposition", *Nano Lett.*, 9(1), 30 (2008).
7. X. Li, W. Cai, J. H. An, S. Y. Kim, J. H. Nah, D. Yang, R. Piner, A. Velamakanni, I. H. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff, "Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils", *Science.*, 324(5932), 1312 (2009).
8. K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi and B. H. Hong, "Large-scale pattern growth of graphene films for stretchable transparent electrodes", *Nature.*, 457(7230), 706 (2009).
9. S. Chen, L. Brown, M. Levendorf, W. Cai, S.-Y. Ju, J. Edgeworth, X. Li, C. W. Magnuson, A. Velamakanni, R. D. Piner, J. Y. Kang, J. W. Park and R. S. Ruoff, "Oxidation resistance of graphene-coated Cu and Cu/Ni alloy", *ACS nano.*, 5(2), 1321 (2011).
10. S.-E. Zhu, R. Shabani, J. Rho, Y. Kim, B. H. Hong, J.-H. Ahn and H. J. Cho, "Graphene-based bimorph microactuators", *Nano letters.*, 11(3), 977 (2011).
11. L. G. Martins, Y. Song, T. Zeng, M. S. Dresselhaus, J. Kong and P. T. Araujo, "Direct transfer of graphene onto flexible substrates", *Proceedings of the National Academy of Sciences of the United States of America.*, 110(44), 17762 (2013).
12. J. Song, F.-Y. Kam, R.-Q. Peng, W.-L. Seah, J.-M. Zhuo, G.-K. Lim, P. K. H. Ho and L.-L. Chua, "A general method for transferring graphene onto soft surfaces", *Nature Nanotechnology.*, 8(5), 356-362 (2013).
13. D. Y. Wang, I. S. Huang, P. H. Ho, S. S. Li, Y. C. Yeh, D. W. Wang, W. L. Chen, Y. Y. Lee, Y. M. Chang, C. C. Chen, C. T. Liang and C. W. Chen, "Clean-Lifting Transfer of Large-area Residual-Free Graphene Films", *Advanced Materials.*, 25(32), 4521 (2013).
14. J. Kang, S. Hwang, J. H. Kim, M. H. Kim, J. Ryu, S. J. Seo, B. H. Hong, M. K. Kim and J. B. Choi, "Efficient Transfer of Large-Area Graphene Films onto Rigid Substrates by Hot Pressing", *ACS nano.*, 6(6), 5360 (2012).
15. V. P. Verma, S. Das, I. Lahiri and W. Choi, "Large-area graphene on polymer film for flexible and transparent anode in field emission device", *Applied Physics Letters.*, 96(20), 203108 (2010).
16. T. Kobayashi, M. Bando, N. Kimura, K. Shimizu, K. Kadono, N. Umez, K. Miyahara, S. Hayazaki, S. Nagai, Y. Mizuguchi, Y. Murakami and D. Hobar, "Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process", *Appl. Phys. Lett.*, 102(2), 0231120 (2013).
17. X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R. D. Piner, L. Colombo and R. S. Ruoff, "Transfer of Large-Area Graphene Films for High-Performance Transparent Conductive Electrodes", *Nano Lett.*, 9(12), 4359 (2009).
18. S. U. Jo, H. J. Kang and M. Y. Jeong, "The Study of Optical Device embedded Optical Alignment fabricated by Roll to Roll Process", *J. Microelectron. Packag. Soc.*, 20(3), 19 (2013).
19. M. K. Lee, E. K. Lee, M. Yang, M. W. Chon, H. Lee, J. S. Lim and S. H. Choa, "Flexibility Study of Silicon Thin Film Transferred on Flexible Substrate", *J. Microelectron. Packag. Soc.*, 20(3), 23 (2013).
20. Y. Wang, Y. Zheng, X. Xu, E. Dubuisson, Q. Bao, J. Lu and K. P. Loh, "Electrochemical Delamination of CVD-Grown Graphene Film: Toward the Recyclable Use of Copper Catalyst", *ACS Nano.*, 5(12), 9927 (2011).
21. L. Gao, W. Ren, H. Xu, L. Jin, Z. Wang, T. Ma, L.-P. Ma, Z. Zhang, Q. Fu, L.-M. Peng, X. Bao and H.-M. Cheng, "Repeated growth and bubbling transfer of graphene with millimetre-size single-crystal grains using platinum", *Nature Communications.*, 3(699), 1 (2012).
22. E. H. Lock, M. Baraket, M. Laskoski, S. P. Mulvaney, W. K. Lee, P. E. Sheehan, D. R. Hines, J. T. Robinson, J. Tosado, M. S. Fuhrer, S. C. Hernández and S. G. Walto, "High-Quality Uniform Dry Transfer of Graphene to Polymers", *Nano Lett.*, 12(1), 102 (2011).
23. C. Kim, J. Y. Woo, J. Choi, J. Park and C.-S. Han, "Direct transfer of graphene without the removal of a metal substrate using a liquid polymer", *Scripta Materialia.*, 66(8), 535 (2012).
24. T. Yoon, W. C. Shin, T. Y. Kim, J. H. Mun, T.-S. Kim and B. J. Cho, "Direct Measurement of Adhesion Energy of Monolayer Graphene As-Grown on Copper and Its Application to Renewable Transfer Process", *Nano Lett.*, 12(3), 1448 (2012).
25. Z. Suo and J. W. Hutchinson, "Interface crack between two elastic layers", *International Journal of Fracture.*, 43(1), 1 (1990).
26. J. W. Hutchinson and Z. Suo, "Mixed Mode Cracking in Layered Materials", *Advances in Applied Mechanics.*, 29(63), 191 (1992).
27. A. Kamer, K. Larson-Smith, L. S. C. Pingree and R. H. Dauskardt, "Adhesion and degradation of hard coatings on

- poly (methyl methacrylate) substrates”, *Thin Solid Films.*, 519(6), 1907 (2011).
28. S. P. Koenig, N. G. Boddeti, M. L. Dunn and J. S. Bunch, “Ultrastrong adhesion of graphene membranes”, *Nature nanotechnology.*, 6(9), 543 (2011).
29. M. Kanninen, “An augmented double cantilever beam model for studying crack propagation and arrest”, *International Journal of Fracture.*, 9(1), 83 (1973).
30. A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K. S. Novoselov, S. Roth and A. K. Geim, “Raman Spectrum of Graphene and Graphene Layers”, *Phys. Rev. Lett.*, 97, 187401 (2006).