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(54) Title: STABLE IR TRANSPARENT CONDUCTIVE GRAPHENE HYBRID MATERIALS AND METHODS OF MAKING

(57) Abstract: A method of making a transparent conductive graphene hybrid, comprising the steps of providing a PMMA/Graphene hybrid, functionalizing the PMMA/Graphene hybrid, providing a transparent substrate, oxidizing the transparent substrate, treating the oxidized substrate and forming a functionalized substrate, applying the PMMA/Graphene hybrid to the functionalized substrate, removing the PMMA, and forming a transparent conductive graphene hybrid. A transparent conductive graphene hybrid comprising a transparent substrate, wherein the transparent substrate is oxidized, and wherein the transparent substrate is treated with TFPA-NH2 to form a functionalized substrate, and a layer of graphene on the functionalized substrate.

TITLE OF THE INVENTION

Stable IR Transparent Conductive Graphene Hybrid Materials and Methods of Making

REFERENCE TO RELATED APPLICATION

This application is a non-provisional of, and claims priority to and the benefits of, United States Provisional Patent Application Number 62/332,961 filed on May 06, 2016.

BACKGROUND

This disclosure teaches a method to produce conductive IR transparent hybrid materials on organic and inorganic materials without loss of electrical properties over time.

Since its discovery in 2004, a monolayer of sp^2 carbon called graphene, has attracted extensive amount of research (over 14,000 papers with the keyword grapheme). This is due to its extremely high carrier mobility (> 200 000 $cm^2V^{-1}s^{-1}$), a room temperature quantum Hall effect, a tremendously high optical transparency of 97.7 % can capture broader spectrum than conventional semiconducting materials, a high Young's modulus (1 TPa), and extraordinarily large specific surface area of 2630 m^2/g^{-1}. Graphene applications range from high end physics instrumentations, metrology, electronics, spintronics, photonics and optoelectronic devices, sensors, flexible electronics, as well as energy storage devices such as batteries, supercapacitors, solar cells and in biomedical applications as single molecule screening devices, targeted drug delivery systems, etc.

Graphene has attracted a lot of attention for its promise as a transparent conductor. Indeed, depending on the sheet resistance in Ω/sq $inch^{-1}$, it can be used as touch screens (400-500 Ω/sq $inch^{-1}$), smart windows (300-400 Ω/sq $inch^{-1}$), flexible Organic Light Emitting Diode (OLED)/Liquid Crystal Display (LCD) displays (25-300 Ω/sq $inch^{-1}$), and solar cells (1-10 Ω/sq $inch^{-1}$). The state of the art transparent conducting materials (indium tin oxide (ITO) or fluorine doped tin oxide (FTO)) are currently the most expensive parts of a dye-sensitized solar cell. In addition, these oxides are typically deposited at high temperatures beyond the thermal limit of polymers, and their brittleness is a drawback when flexibility is required. For example, resistivity of 100 Ohm/sq was obtained by graphene functionalization with HNO_3.

Although combined low resistivity (< 10 Ω/sq) and high transparency in the graphene transparent conductors has not been achieved yet, graphene has shown promise. Reduction of graphene resistivity to 50 Ohm/sq was obtained by stacking single graphene layers (4 sequential single layer transfers) and then functionalization of the top surface by HNO_3. The lowest reported value was by Hong of 30 Ohm/sq. Other solvents were tried as well - $SoCl_2$, H_2SO_4, nitromethane, HCl. However, the final graphene surfaces are unstable. Bult et.al. discussed the role of dopants on carrier transport for graphene transparent conducting thin films. They used hydrazine doping performed in helium glove box, nitric acid dip and polyethyleneimine in air. They achieved 50 Ohm/sq for 89 % transmission. However, they also show change in electrical performance of hydrazine functionalized devices within 150 seconds of exposure to air. Graphene surface functionalization with diethylenetriamine (DETA) in vapor phase which induces n-type doping was shown by Y. Kim et.al. When this is combined with substrate-induced doping using amine –

functionalized self-assembled covered SiO_2/Si, the group shows that graphene's sheet resistance is reduced to 86 Ohm/sq. The issue with surface stability was not analyzed.

SUMMARY OF DISCLOSURE

Description

This disclosure pertains to a conductive IR transparent hybrid material on organic and inorganic materials without loss of electrical properties over time, and methods of making.

DESCRIPTION OF THE DRAWINGS

The following description and drawings set forth certain illustrative implementations of the disclosure in detail, which are indicative of several exemplary ways in which the various principles of the disclosure may be carried out. The illustrated examples, however, are not exhaustive of the many possible embodiments of the disclosure. Other objects, advantages and novel features of the disclosure will be set forth in the following detailed description when considered in conjunction with the drawings.

Fig. 1A is a schematic of one step graphene transfer.

Fig. 1B is a schematic of a modified one step graphene transfer.

Figure 2 illustrates electrical and optical properties of graphene/Al_2O_3 hybrid materials after one step graphene transfer of single and multilayer graphene.

Figure 3 illustrates comparison of sheet resistance of graphene/Al_2O_3 as a function of number of graphene layers and Al_2O_3 surface induced doping.

Figure 4 illustrates transmission of graphene/Al_2O_3 as a function of number of graphene layers and Al_2O_3 surface induced doping.

Figure 5 illustrates comparison of sheet resistance of graphene/Ge as a function of number of graphene layers and Ge surface induced doping.

Figure 6 illustrates transmission of graphene/Ge as a function of number of graphene layers and Ge surface induced doping in the IR wavelengths 4 μm and 9 μm.

Fig. 7A is a schematic of sequential graphene transfer.

Fig. 7B is a schematic of modified sequential graphene transfer.

Figure 8 illustrates optical and electrical measurements of Gr/Al_2O_3 hybrid materials obtained using sequential transfer method. Sample 1 was prepared by using 2L/2L graphene on $Al2O_3$ sample, functionalizing it with TFPA and then transferring 3L bottom functionalized graphene with HNO_3 onto it. Sample 2 was prepared by using 2L/2L graphene on $Al2O_3$ sample, functionalizing it with TFPA and then transferring 3L bottom functionalized graphene with HNO_3 onto it and then functionalizing the top surface with TFPA. Sample 3 was prepared by using 6L graphene on $Al2O_3$ sample, functionalizing it with TFPA and then transferring 1L bottom functionalized graphene with HNO_3 onto it.

Sample 4 was prepared by using 3L graphene on $Al2O_3$ sample, functionalizing it with TFPA and then transferring 2L bottom functionalized graphene with HNO_3 onto it. Sample 5 was prepared by using 2L graphene on $Al2O_3$ sample, functionalizing it with TFPA and then transferring 3L bottom functionalized graphene with HNO_3 onto it.

Figure 9 illustrates optical and electrical measurements of Gr/Ge hybrid materials obtained using sequential transfer method. Sample 1 was prepared by placing 6L of graphene Ge, functionalizing graphene on Ge and then transfer 1L bottom functionalized graphene with HNO3 onto it. Sample 2 was prepared by using 2L/2L graphene on Ge sample, functionalizing it and then transferring 3L bottom functionalized graphene with HNO_3 onto it. Sample 3 was prepared by using 3L graphene, functionalizing it by TFPA and then transferring 2L bottom functionalized graphene with HNO_3 onto it.

Figure 10 illustrates transmission of Al_2O_3 and Ge reference and Gr/Al_2O_3 and Gr/Ge hybrid materials in the IR wavelengths.

Figure 11 illustrates sheet resistance measurements of Gr/Al_2O_3 nine months after graphene transfer.

DETAILED DESCRIPTION OF THE INVENTION

A stable IR transparent conductive graphene hybrid material, and methods of making, are disclosed herein. The conductive graphene hybrid materials are without loss in electrical properties over time.

The proof of concept experiments were performed with commercially available graphene (Gr) grown by chemical vapor deposition on Cu foils. Both single and multilayer graphene (2 layers, 3-5 layers, 6-8 layers from ACS Materials) were used. The transparent substrates used were sapphire and germanium wafer (doubly polished). However, the proposed method is applicable to any transparent substrate (organic and inorganic), considering that its surface needs to be oxidized before transfer to enhance adhesion of graphene to it.

To produce graphene-based hybrid material, graphene must be removed from the Cu foil and placed onto the substrate of interest. Different methods have been developed to achieve this result. They can generally be divided into dry and wet chemical approaches. The wet chemical methods rely on wet chemical etch of the Cu foil, while the top surface of the graphene is preserved by a sacrificial polymeric layers. The main drawback is cleaning of the polymeric residue from the graphene surface on atomic scale. The dry approaches reply on mechanical peeling of the graphene without exposure to chemicals. Lock et. al. discovered a method that relies on differential adhesion with the basic idea that if the graphene's adhesion to the target substrate is higher than the adhesion between graphene and the Cu foil, graphene would be transferred (US Patent Application Number 13/466,248). In this work, wet chemical approach was used as explained below. However, the same concept can be applied using a dry transfer approach as well.

Example 1

In the wet chemical approach both one step transfer and multiple sequential transfers were used. Schematics of the one step graphene transfer (OSGT) and the modified one step graphene transfer (MOSGT) methods are shown in Figure 1. In the one step graphene transfer, graphene surfaces was coated by PMMA at 4000 rpm for 1 min, then placed in APS 100 Cu etchant for 8 hours. Then the PMMA/Gr hybrid was placed in deionized water for 12 hours to rinse the metal residues from the graphene surface. Separately, the surface of the transparent substrate was treated chemically or by plasma to produce highly oxidized surface. Germanium surface was plasma functionalized using microwave Plasma Preen System in argon or oxygen environment for 1 minute. The sapphire was first immersed into sc1 solution for 10 minutes (DI H_2O:H_2O_2:NH_4OH 6:1.5:1 80 °C), followed by HF etch for 1 minute (49 % HF in H_2O 1:100) and sc2 incubation (H_2O:$H2O_2$:HCl 7:1.5:1 80 °C) for 10 minutes. Then, the PMMA/Gr hybrid was scooped with the modified target surface. Then, the PMMA/Gr/substrate was placed on hot plate at 60 °C for a few minutes, followed by bake at 120 °C for 1 minute. The PMMA film was removed by acetone dip for 1 minute, followed by rinse in isopropanol and dried with nitrogen. In the MOSGT transfer, the effect of functionalization of target surface on graphene's electrical properties was explored. The oxidized target substrates (UHMW PE, sapphire and germanium) were further functionalized with TFPA-NH_2 solution in methanol by dip coating for two hours. This functionalization can be expanded to other chemical, plasma-based functionalizations as well as target surface modification by self assembled monolayers (e.g. silane- based).

The electrical and optical properties of graphene/Al_2O_3 hybrids produced by the one step transfer of single and multilayer graphene are shown in Figure 2. It should be noted that the graphene surface is very sensitive to polymeric residues after the transfer, as well as to its post-treatment. Methanol rinse increased the sheet resistance of the single and double layer graphene surfaces. Additional annealing step in Ar/H_2 mixture was needed to reduce their resistance values. The obtained resistance values were in the kΩ/sq range. The lowest values were obtained using 6 layers graphene 800 Ω/sq. The transmission of the Gr/Al_2O_3 hybrid was reduced proportional to the number of the graphene layers.

Multiple attempts were made to optimize the OSGT by use of different PMMA resists, and methods for PMMA removal. The best results are shown in Figure 3 – lower resistivity values were obtained for the transfer of single and double layers of graphene (1.5 kΩ/sq). The multilayers (3L, 6L) were not affected. In further attempt to minimalize the resistance of the Gr/Al_2O_3 hybrids the MOSGT method was applied. As shown in Figure 3, the resistance of double layer graphene sample was further reduced. The transmission values of the graphene/Al_2O_3 produced by this method are shown in Figure 4 suggest that substrate functionalization dos not significantly affect the optical properties of the hybrids.

Figure 5 shows the results from the OSGT and MOSGT transfer of single and multilayer graphene to germanium. The obtained resistance values were in the kΩ/sq range with the lowest value achieved when 6L of graphene was used consistent with previous results. The functionalization of germanium did not decrease the sheet

resistance values of graphene as was the case with Al_2O_3. Transmission of germanium and Gr/germanium hybrids after the OSGT and MOSGT methods at two wavelengths (4 and 9 μm) are shown in Figure 6 – insignificant decrease of transmission (3-4 %) was observed in Gr/Ge hybrids compared to Ge reference. In summary single layer transfer of graphene resulted in obtaining conductive Gr/Al_2O_3 and Gr/Ge hybrids with the sheet resistance 1-3 kΩ/sq.

Example 2

To further lower the resistance of the hybrid materials, the sequential transfer protocols were developed. First, graphene layers were sequentially placed on top of each other (SGT) following the OSGT protocols explained above. However, this approach did not yield the desired results. For this reason, in the modified sequential transfer protocol shown in Figure 7, an additional step after the water rinsing of graphene to functionalize the bottom of the graphene in 2M HNO_3 solution in water (note the top graphene surface is protected with PMMA layer). Then, this functionalized surface is contacted with functionalized transparent surface (with TFPA-NH_2 molecules) and hydrogen bonds between the oxygen functional groups of graphene and NH_2 functionalities of the substrates are created. For sequential placement, the top graphene surface is functionalized by TFPA-NH_2 as well.

The electrical and optical results of sequential graphene transfer to Al_2O_3 are shown in Figure 8 respectively. The sheet resistance values below 300 W/sq were achieved. Also, we found that the order in which graphene is layered mattered (2L/3L vs. 3L/2L; 2L/2L/3L vs 6L/1L). Even though the total number of layers is the same- five layers - 3L/2L had 250 Ohm/sq resistance vs. 100 Ohm/sq of 2L/3L. Similarly 2L/2L/3L had 300 Ohm/sq resistance vs. 200 Ohm/sq resistance 6L/1L. The overall reduction of transmission was less than 10 %, however the resistance values of Gr/Al_2O_3 approach ITO/Al_2O_3 values. The lowest obtained value was 100 Ohm/Sq.

To show to broad applicability of the proposed above approach, similar graphene layering experiments were conducted using germanium as well. Sheet resistance values below 600 Ohm/sq were achieved as well. The dependence of the way graphene layers were placed on the final resistance values was observed as well. Even though the total number of layers is the same (seven), when 6L/1L layered, the hybrid resistance was halves from 600 to 300 Ohm/ in comparison to the 2L/2L/3L combination (Figure 9). The transmission difference for these samples was insignificant, as shown in Figure 9.

In transmission spectra of insulators Al_2O_3 and Ge and the conducting Gr/Al2O3 and Gr/Ge are shown in Figure 10. It is obvious, that the price in transmission is less than 10 % over the whole IR range. The lowest obtained sheet resistance for the Al_2O_3 case was 100 Ohm/sq and for Ge 300 Ohm/sq. Applying the same method using different graphene layering combinations could further reduce these resistance values.

The same strategy can be applied in combination with the Lock et al. developed dry graphene transfer approach. The modified target substrates can be placed to HNO_3 modified graphene/Cu foil in the Nanoimprinter.

After transfer print at 500 psi and 30 minutes, graphene can be removed from Cu foil. Then, graphene's top surface can be modified by TFPA-NH_2 to yield NH_2 functionalized surface and contacted again to HNO_3 modified graphene/Cu foil in the Nanoimprinter for sequential print.

The main drawback of the technologies developed to date is that the electrical resistance of chemically modified substrates degrades with time (seconds to minutes) after functionalization. To evaluate the stability of our samples, nine months after preparation, electrical and optical measurements on small subset of the Gr/Al_2O_3 and Gr/Ge was conducted. The results of electrical measurements are summarized in Figure 11. It is clear that the sheet resistance values are similar to their original values. Thus, the hybrid materials, prepared using this methodology, have surfaces with stable electrical properties. The optical transparent properties were not changed as well.

Disclosed herein are conductive IR transparent substrates with electrical properties that do not degrade over time.

The above examples are merely illustrative of several possible embodiments of various aspects of the present disclosure, wherein equivalent alterations and/or modifications will occur to others skilled in the art upon reading and understanding this specification and the annexed drawings. In addition, although a particular feature of the disclosure may have been illustrated and/or described with respect to only one of several implementations, such feature may be combined with one or more other features of the other implementations as may be desired and advantageous for any given or particular application. Also, to the extent that the terms "including", "includes", "having", "has", "with", or variants thereof are used in the detailed description and/or in the claims, such terms are intended to be inclusive in a manner similar to the term "comprising".

Claims

What we claim is:

1. A method of making a transparent conductive graphene hybrid, comprising the steps of:
providing a PMMA/Graphene hybrid;
functionalizing the PMMA/Graphene hybrid;
providing a transparent substrate;
oxidizing the transparent substrate and forming an oxidized substrate;
treating the oxidized substrate and forming a functionalized substrate;
applying the PMMA/Graphene hybrid to the functionalized substrate;
removing the PMMA; and
forming a transparent conductive graphene hybrid.

2. The method of making a transparent conductive graphene hybrid of claim 1wherein said step of treating the oxidized substrate comprises TFPA-NH2.

3. The method of making a transparent conductive graphene hybrid of claim 2 wherein said step of oxidizing the transparent substrate and forming an oxidized substrate comprises plasma or chemicals.

4. The method of making a transparent conductive graphene hybrid of claim 3 further including the steps of:
functionalizing the graphene layer on the transparent substrate;
providing a second PMMA/Graphene layer;
functionalizing the second PMMA/Graphene layer;
applying the second PMMA/Graphene layer to the functionalized graphene layer;
removing the PMMA; and
forming a transparent conductive graphene hybrid.

5. The method of making a transparent conductive graphene hybrid of claim 4 wherein said step of functionalizing the second PMMA/Graphene layer comprises TFPA-NH2.

6. The method of making a transparent conductive graphene hybrid of claim 4 wherein said wherein the functionalization comprises target surface modification by self-assembled monolayers.

7. A product of the process of:
providing a PMMA/Graphene layer;
functionalizing the PMMA/Graphene layer;
providing a transparent substrate;
oxidizing the transparent substrate and forming an oxidized substrate;
treating the oxidized substrate with TFPA-NH2 and forming a functionalized substrate;
applying the PMMA/Graphene layer to the functionalized substrate;

removing the PMMA; and

forming a transparent conductive graphene hybrid comprising a graphene layer on a transparent substrate.

8. A transparent conductive graphene hybrid comprising:

a transparent substrate;

wherein the transparent substrate is oxidized;

and wherein the transparent substrate is treated with TFPA-NH2 to form a functionalized substrate;

and

a layer of graphene on the functionalized substrate.

Fig. 1A One Step Graphene Transfer (OSGT)

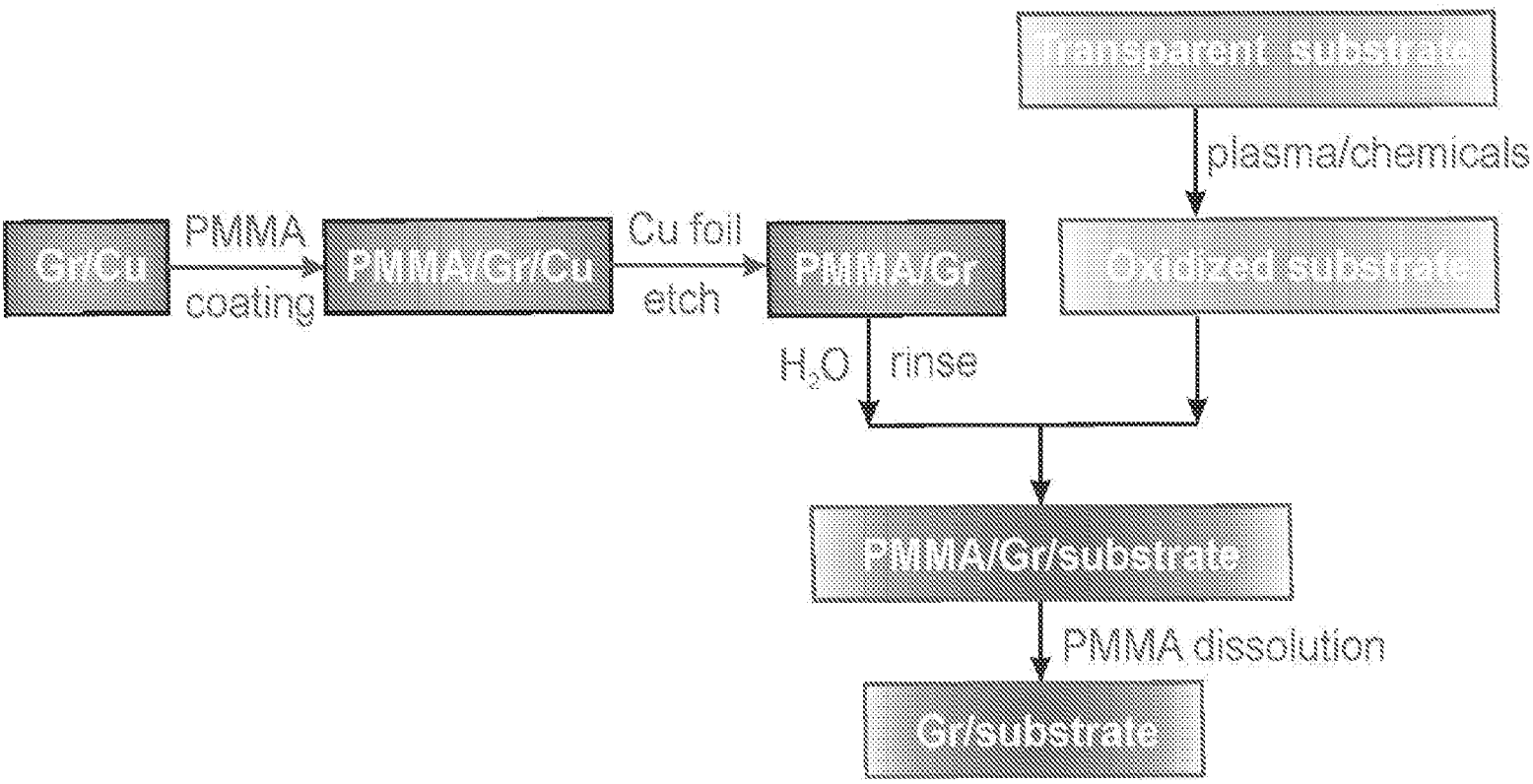
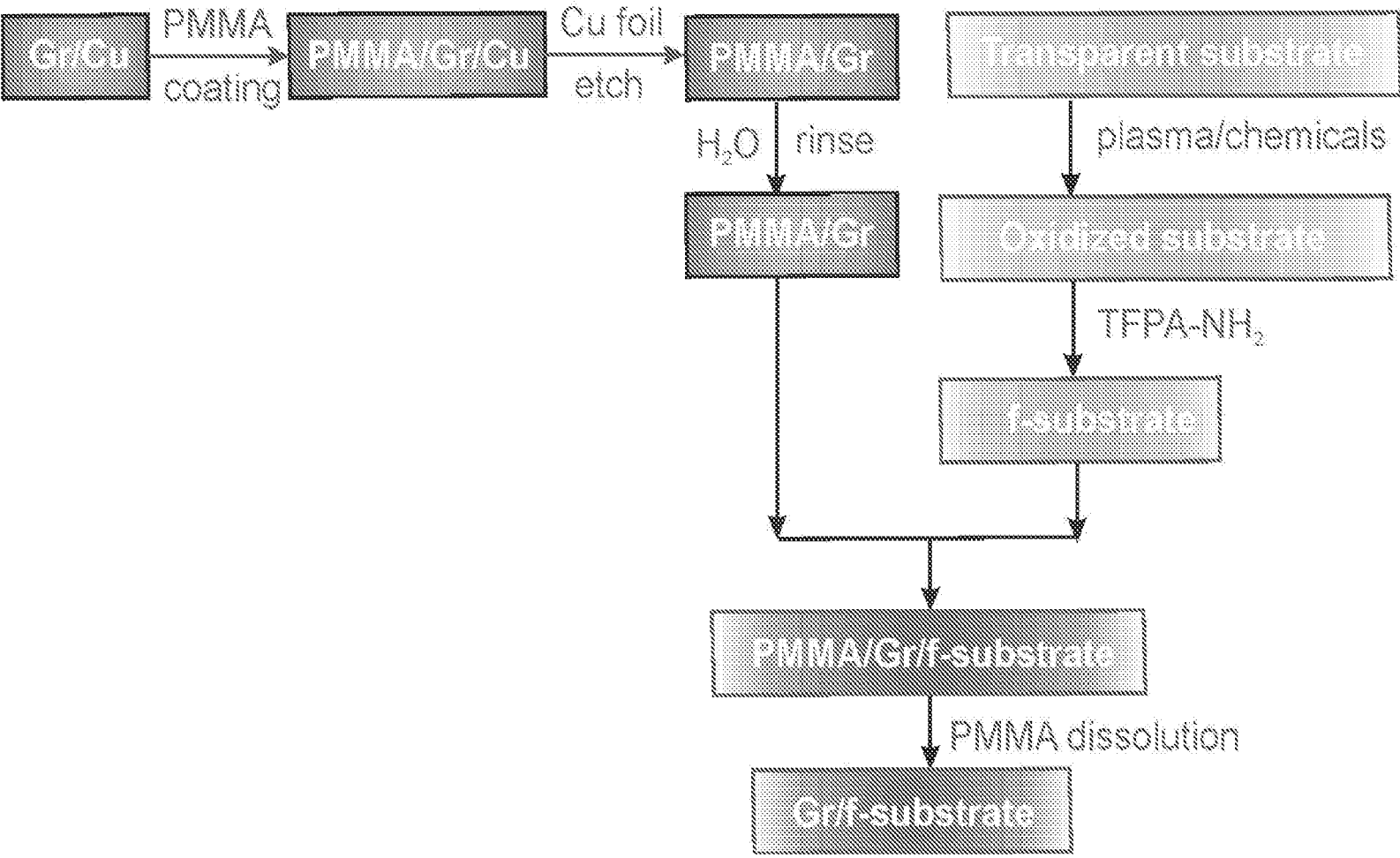


Fig. 1B Modified One Step Graphene Transfer (MOSGT)



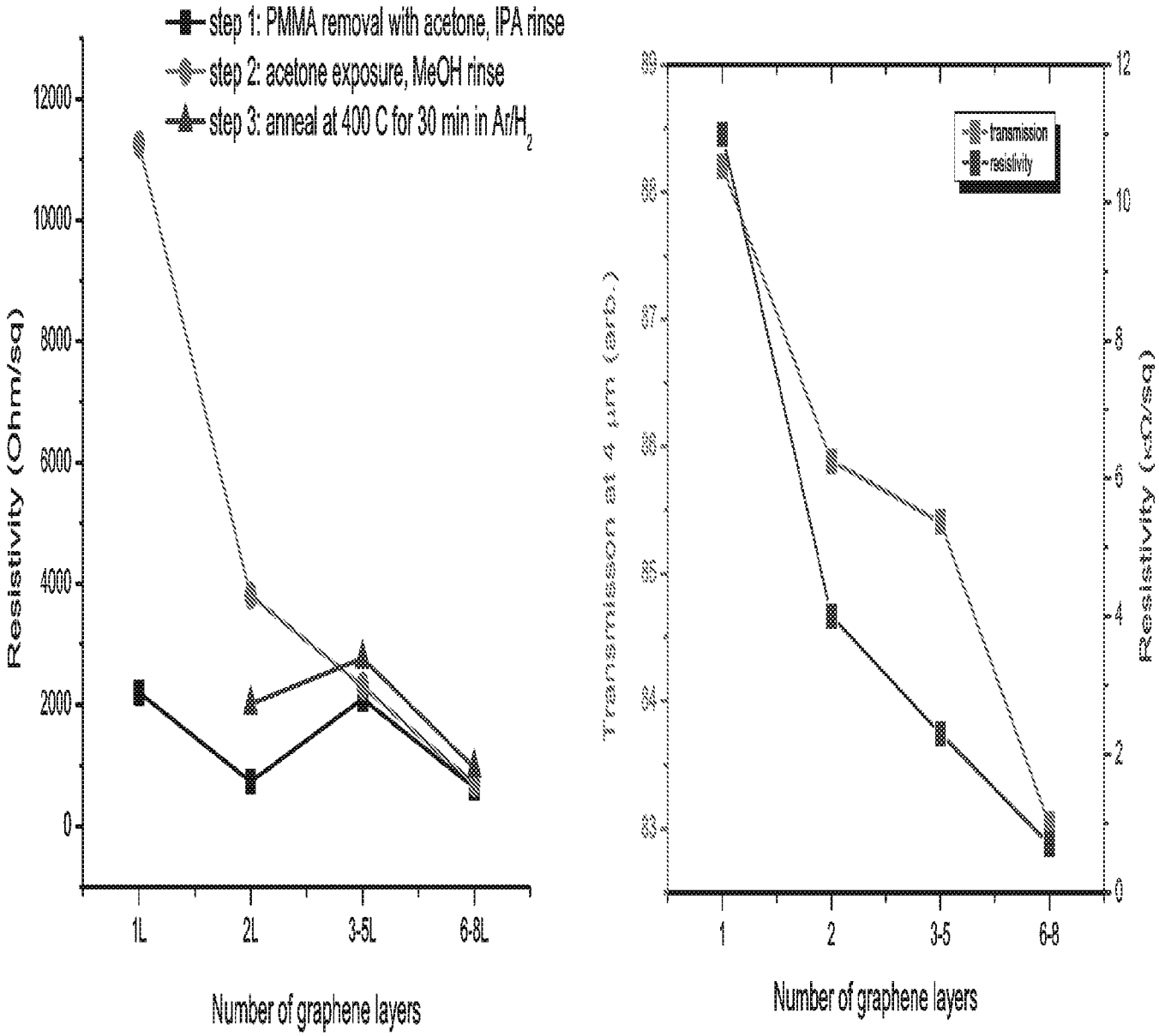

step 1: PMMA removal with acetone, IPA rinse
step 2: acetone exposure, MeOH rinse
step 3: anneal at 400 C for 30 min in Ar/H2
Resistivity (Ohm/sq)
12000
10000
8000
6000
4000
2000
0
1L
2L
3-5L
6-8L
Number of graphene layers
transmission
resistivity
Transmission at 4 um (arb.)
Resistivity (kΩ/sq)
1
2
3-5
6-8
Number of graphene layers

FIGURE 2

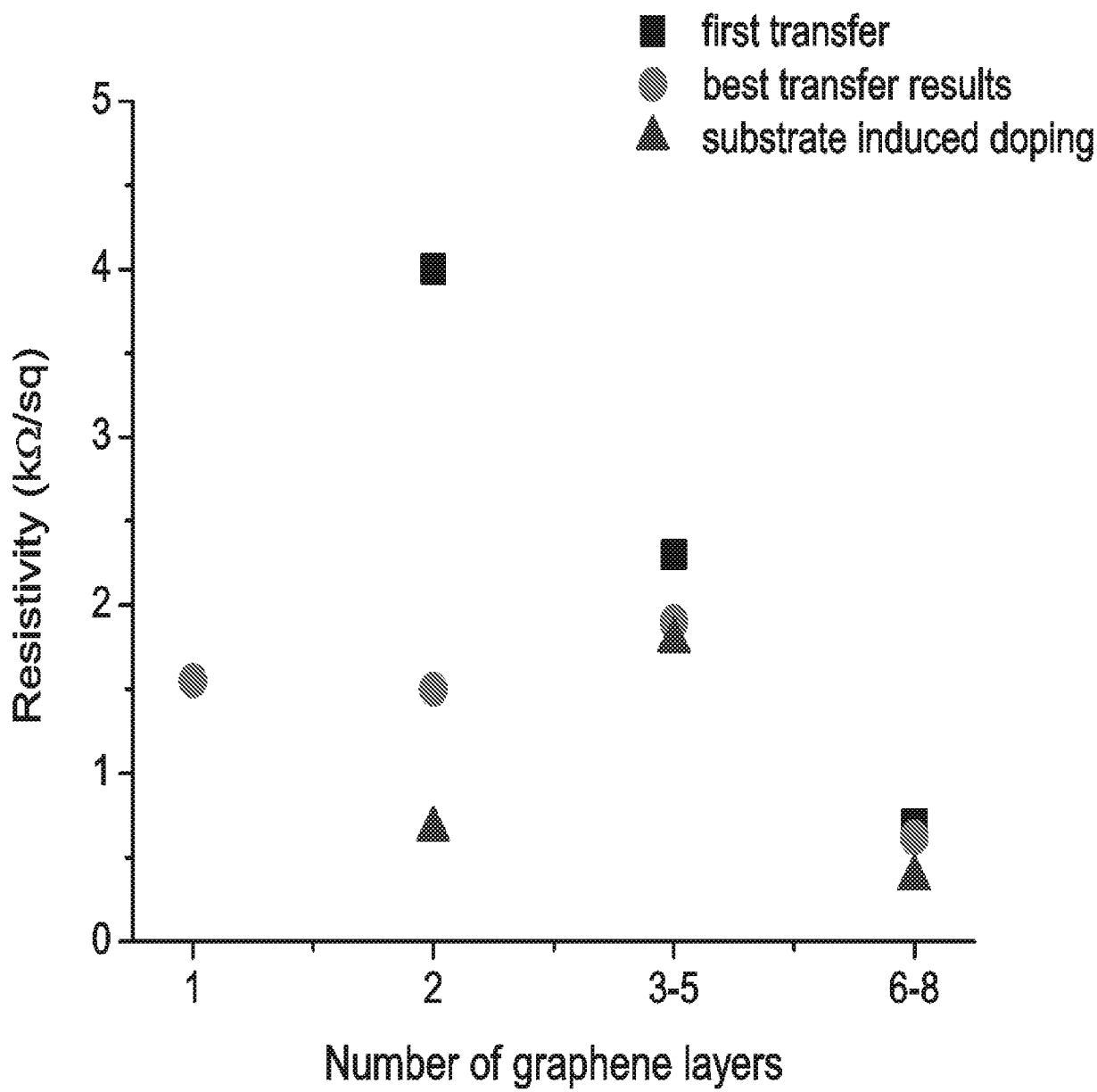

first transfer
best transfer results
substrate induced doping
Resistivity (kΩ/sq)
0
1
2
3
4
5
1
2
3-5
6-8
Number of graphene layers

FIGURE 3

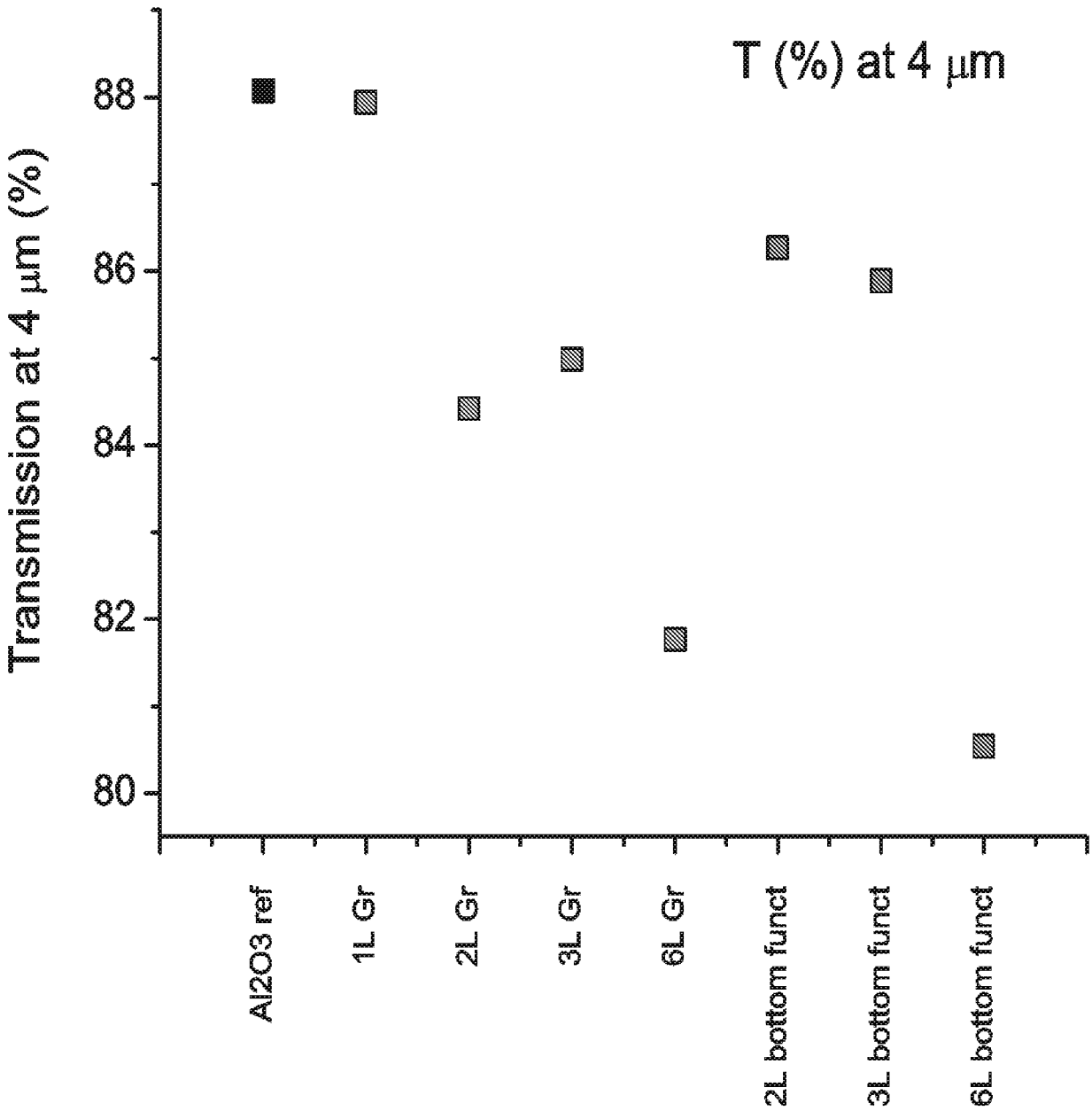

T (%) at 4 μm
Transmission at 4 μm (%)
88
86
84
82
80
Al2O3 ref
1L Gr
2L Gr
3L Gr
6L Gr
2L bottom funct
3L bottom funct
6L bottom funct

FIGURE 4

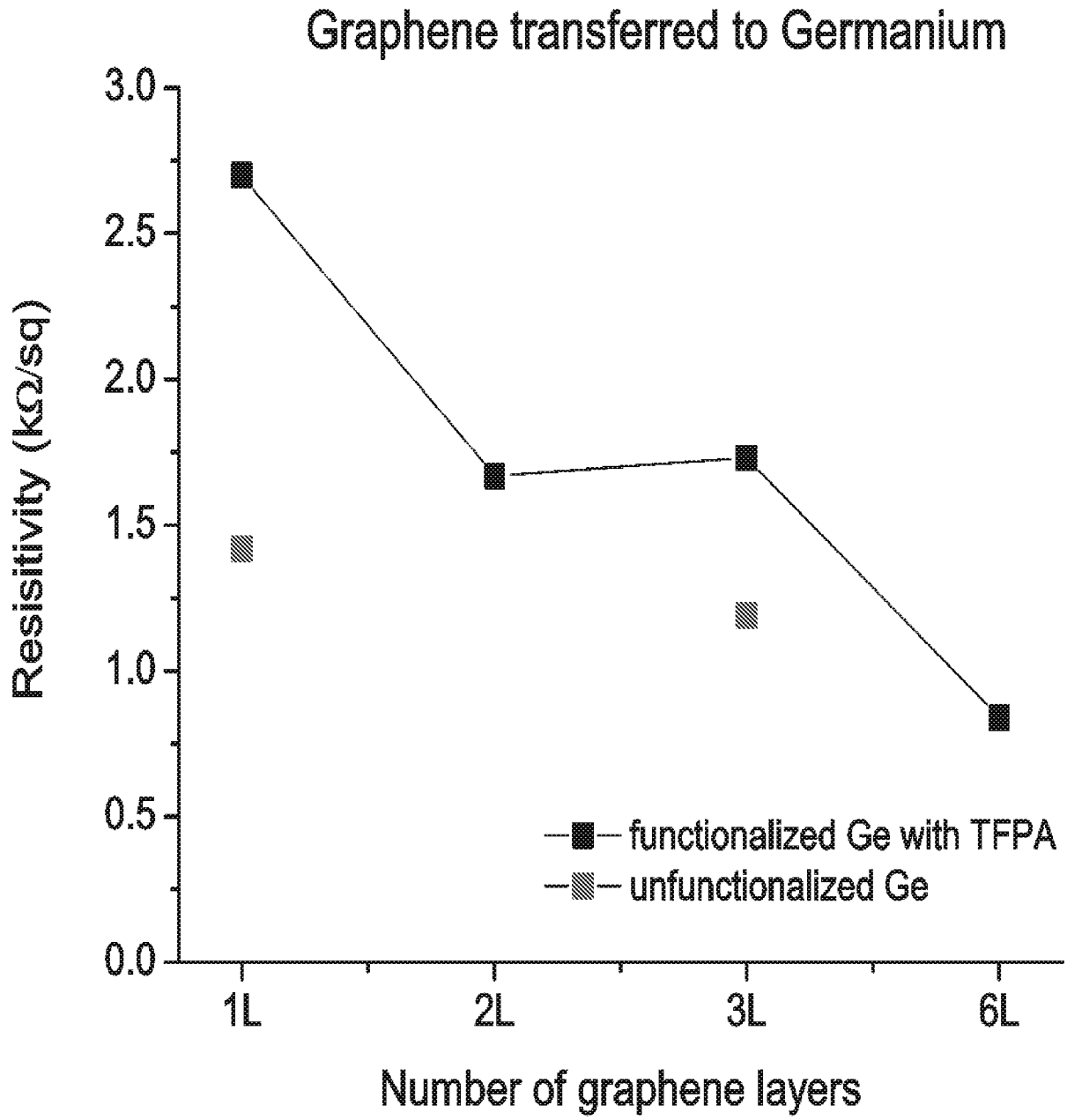
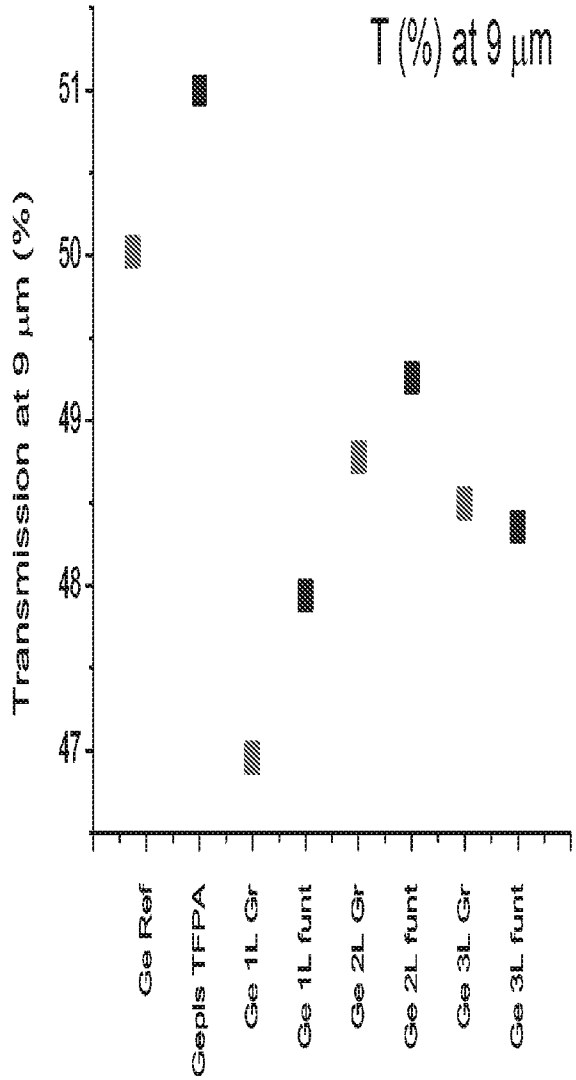

Graphene transferred to Germanium
Resistivity (kΩ/sq)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1L
2L
3L
6L
Number of graphene layers
functionalized Ge with TFPA
unfunctionalized Ge

FIGURE 5


T (%) at 9 µm
Transmission at 9 µm (%)
51
50
49
48
47
Ge Ref
Gepls TFPA
Ge 1L Gr
Ge 1L funt
Ge 2L Gr
Ge 2L funt
Ge 3L Gr
Ge 3L funt

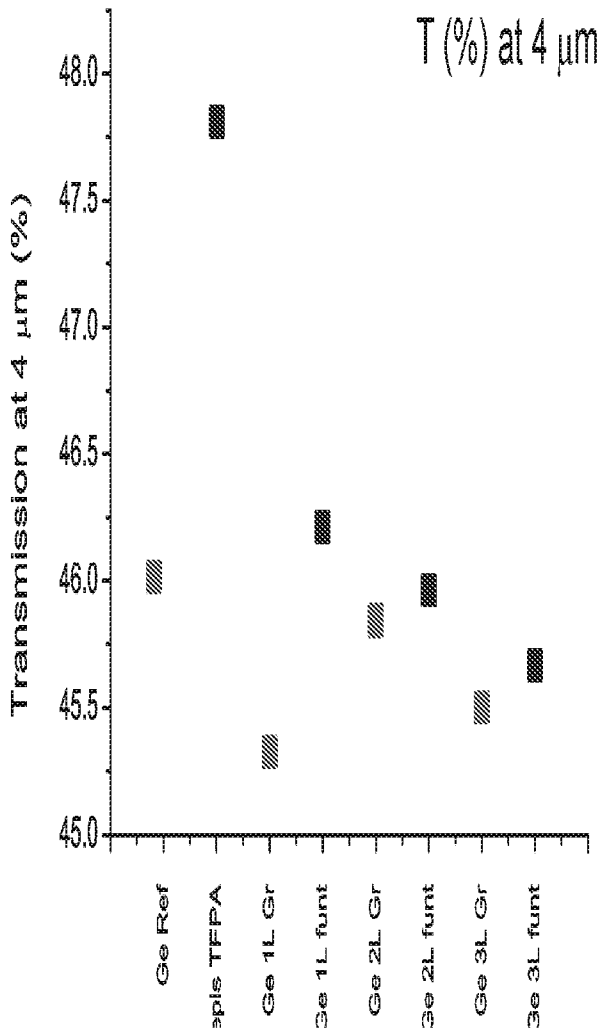

T (%) at 4 µm
Transmission at 4 µm (%)
48.0
47.5
47.0
46.5
46.0
45.5
45.0
Ge Ref
apls TFPA
Ge 1L Gr
3e 1L funt
Ge 2L Gr
3e 2L funt
Ge 3L Gr
3e 3L funt

FIGURE 6

Fig. 7A Sequential Graphene Transfer (SGT)

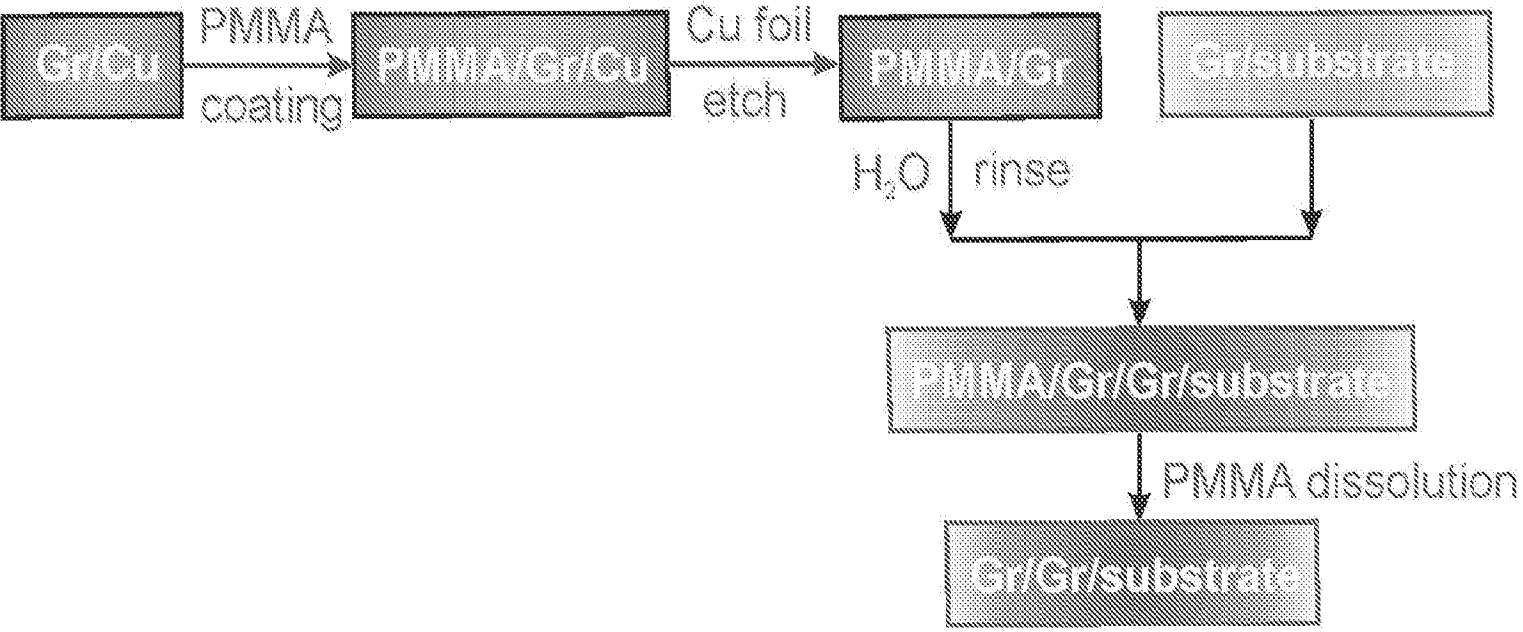
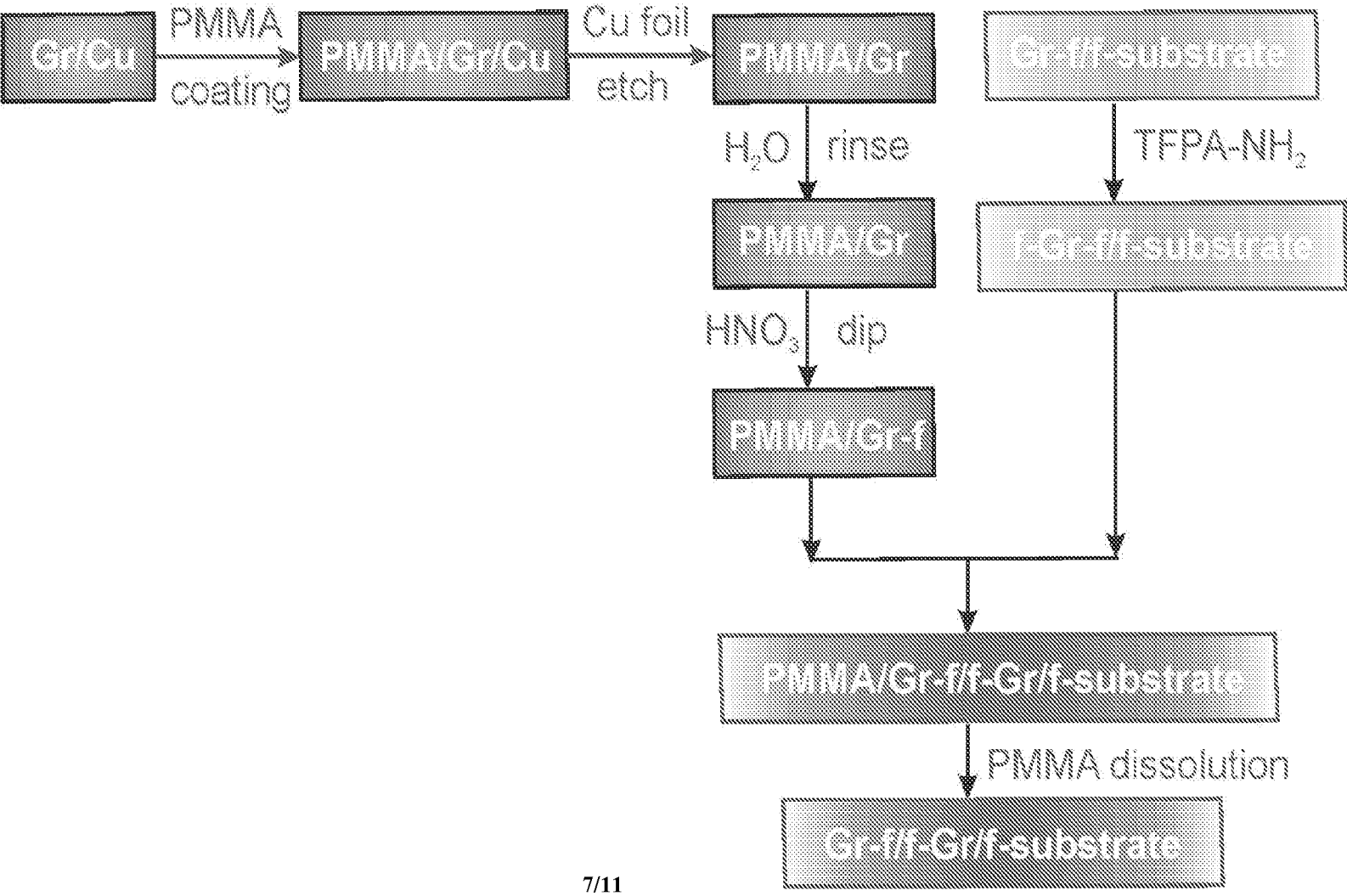


Fig. 7B Modified Sequential Graphene Transfer (MSGT)



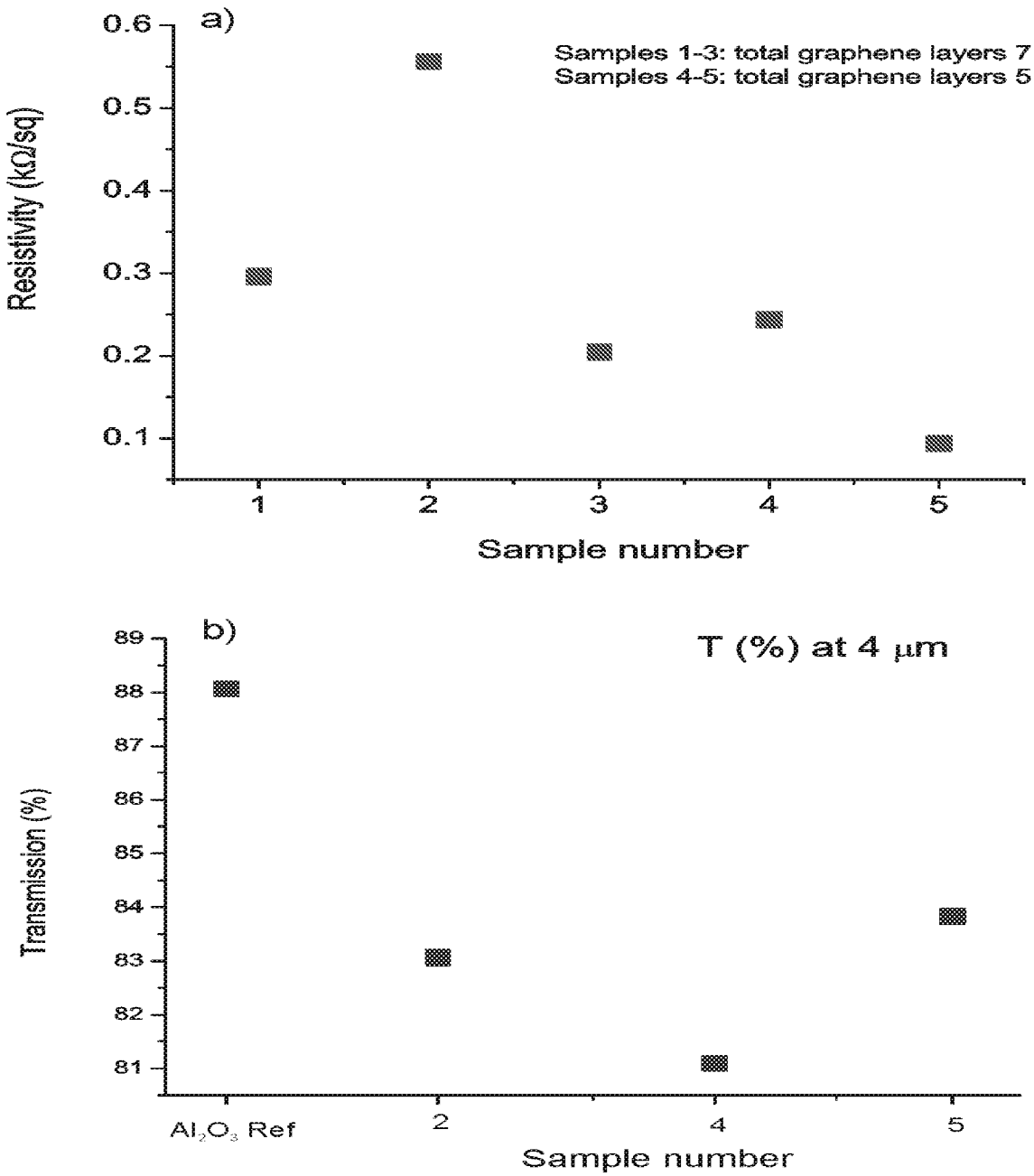

a)
Samples 1-3: total graphene layers 7
Samples 4-5: total graphene layers 5
Resistivity (kΩ/sq)
0.6
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
Sample number
b)
T (%) at 4 μm
Transmission (%)
89
88
87
86
85
84
83
82
81
Al2O3 Ref
2
4
5
Sample number

FIGURE 8

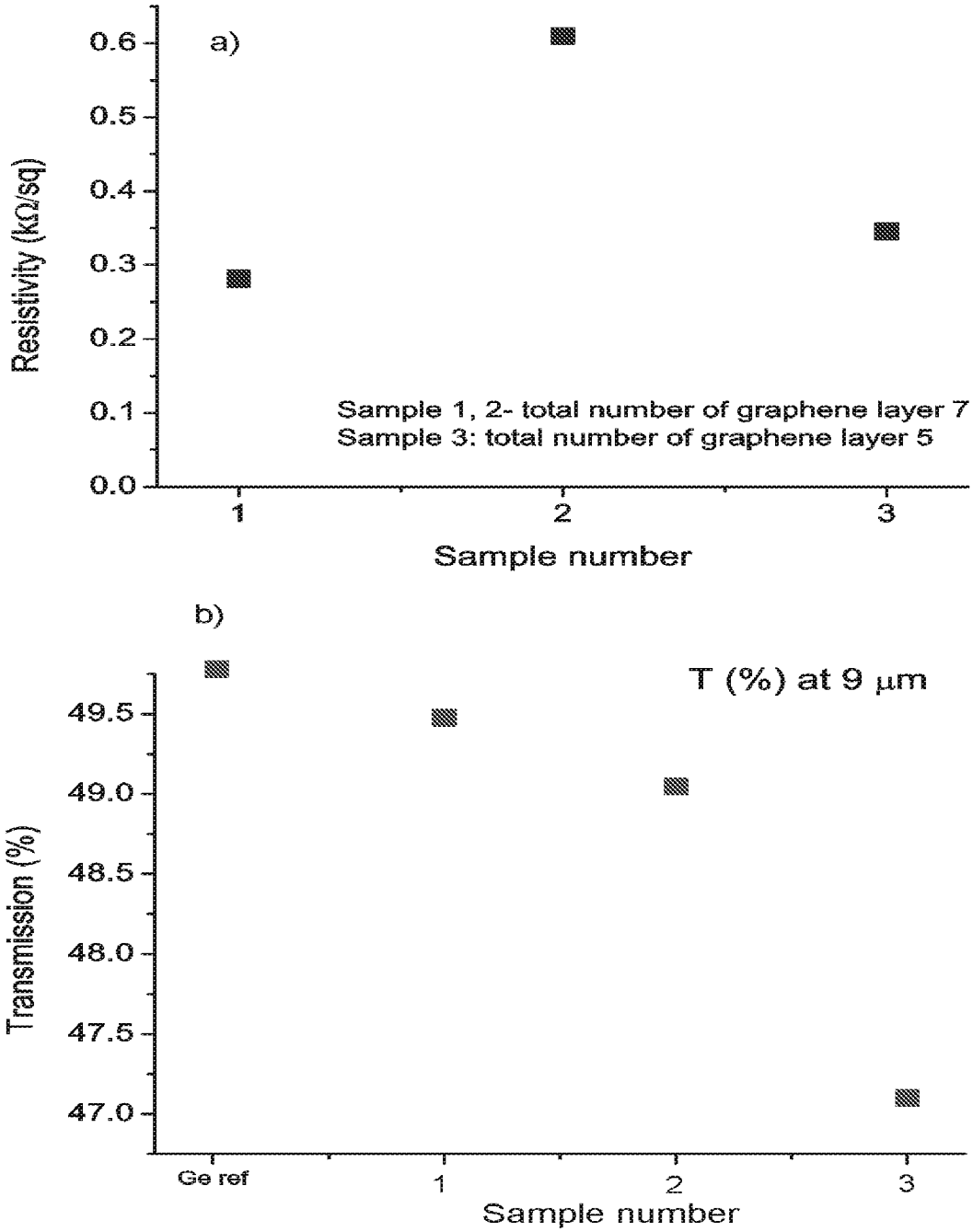

a)
Resistivity (kΩ/sq)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1
2
3
Sample number
Sample 1, 2- total number of graphene layer 7
Sample 3: total number of graphene layer 5
b)
T (%) at 9 μm
Transmission (%)
49.5
49.0
48.5
48.0
47.5
47.0
Ge ref
1
2
3
Sample number

FIGURE 9

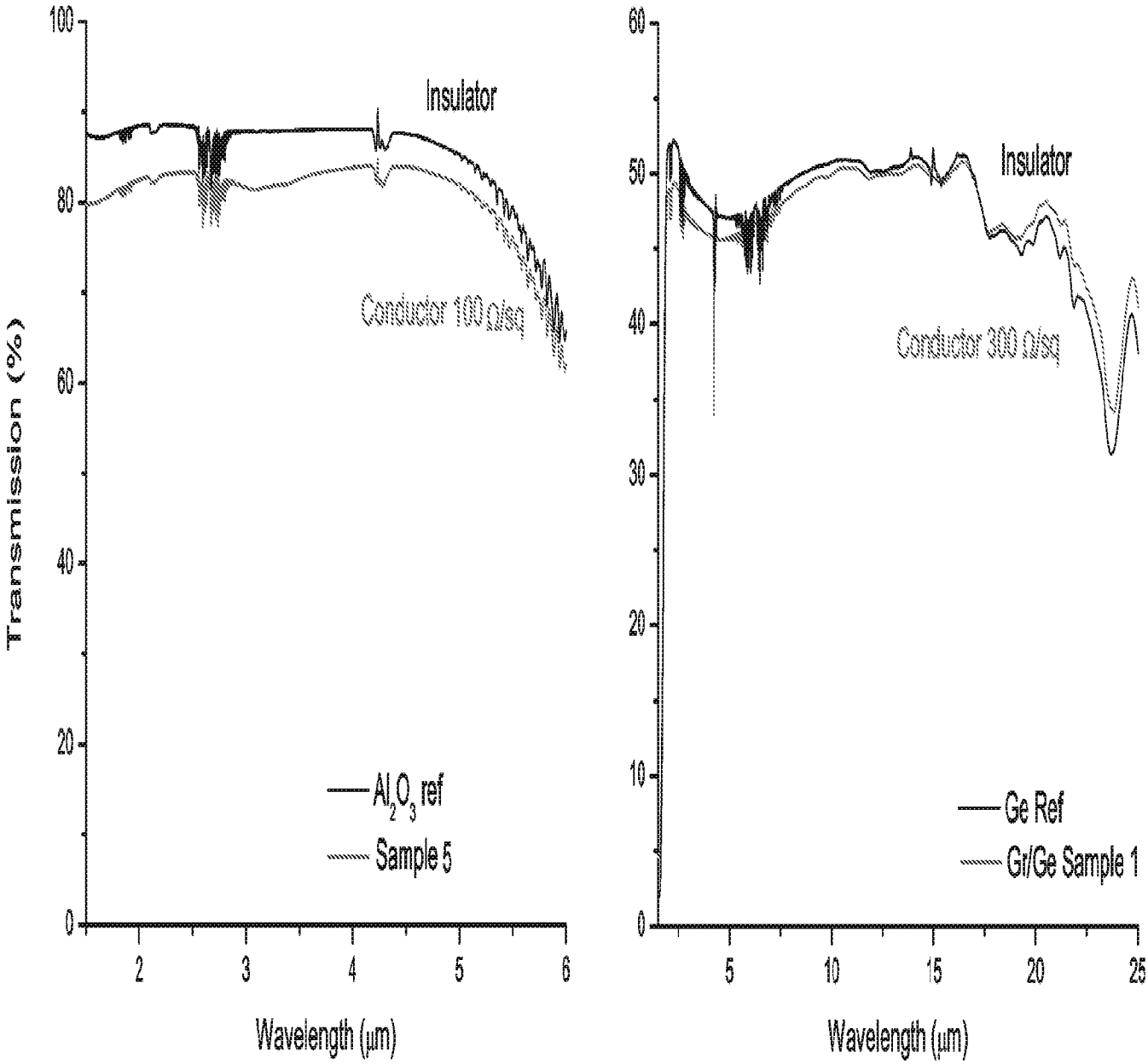

Transmission (%)
Wavelength (μm)
Insulator
Conductor 100 Ω/sq
Al_2O_3 ref
Sample 5
Insulator
Conductor 300 Ω/sq
Ge Ref
Gr/Ge Sample 1

FIGURE 10

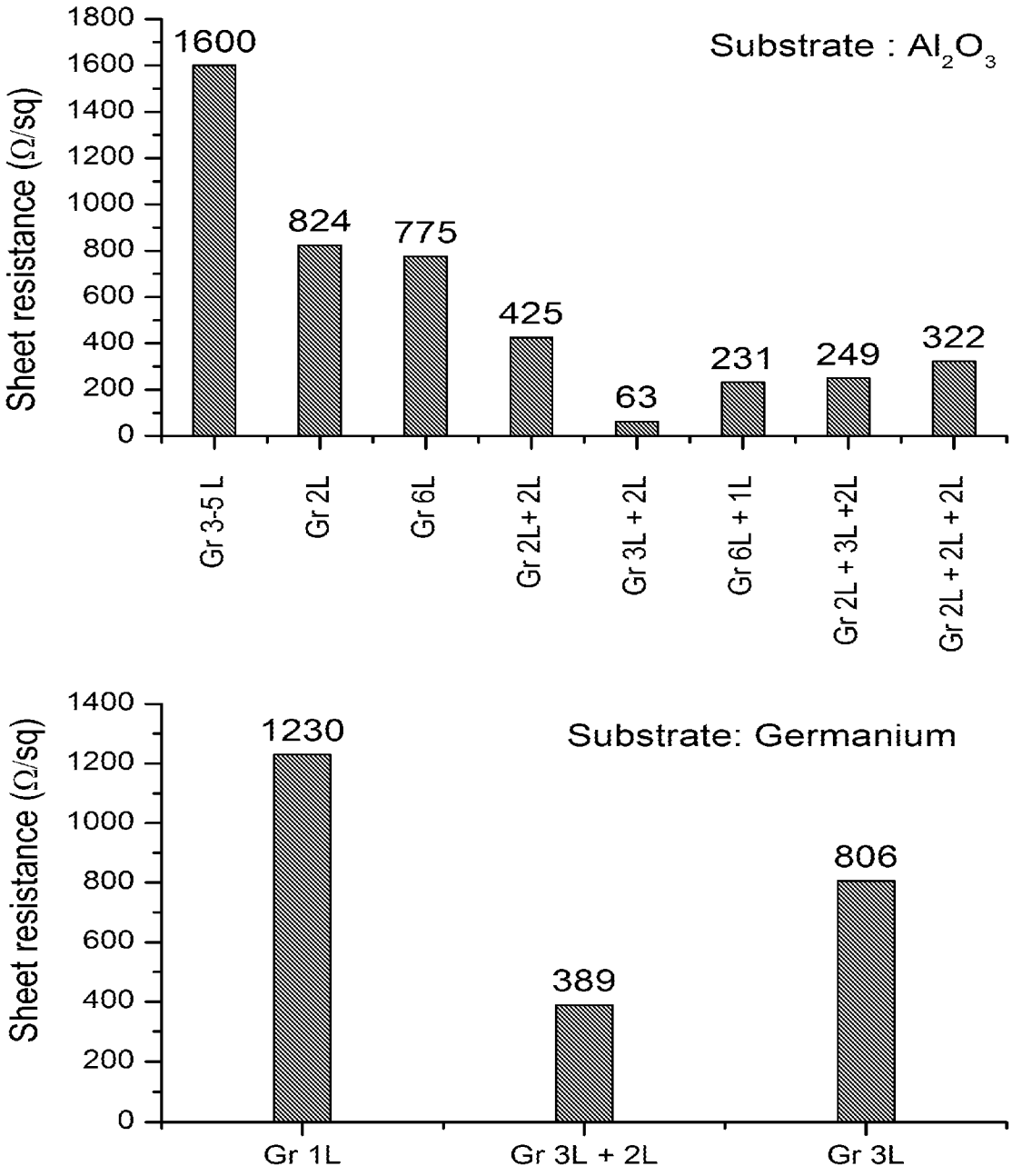


FIGURE 11

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