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(54) Title: *P*-TYPE TRANSPARENT CONDUCTOR WITH REDUCED GRAPHENE OXIDE THIN FILMS AND ONE-STEP SYNTHESIS THEREOF

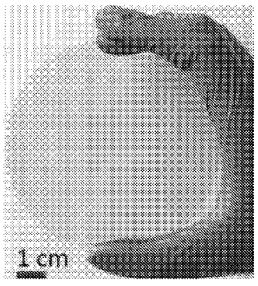


Figure 1a

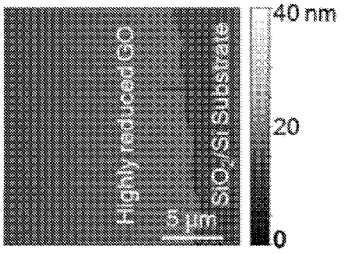


Figure 1b

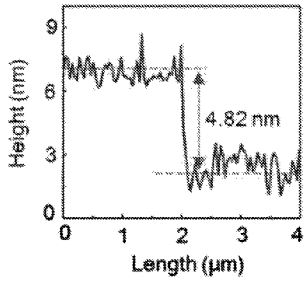


Figure 1c

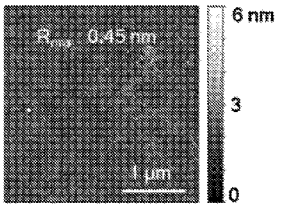


Figure 1d

(57) Abstract: The present invention provides a p-type transparent conductor with deposition of a large area highly reduced graphene oxide thin film by pulsed laser deposition method. The present invention provides a direct growth of large-area wafer-scale reduced graphene oxide thin films using control of the growth ambient of pulsed laser deposition (PLD). The said reduced graphene oxide thin film is directly grown on the substrate by pulsed laser deposition in a reduced atmosphere. The highly reduced graphene oxide thin films of the present invention outperform the chemically grown reduced graphene oxide in their performance as p-type transparent conductors. The highly reduced graphene oxide thin also exhibits a very high transmittance value while simultaneously maintaining a good electrical conductivity.

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P-type transparent conductor with reduced graphene oxide thin films and one-step synthesis thereof

CROSS - REFERENCE TO RELATED PATENT APPLICATION

The embodiments herein claim the priority of Indian patent application 202141012055 filed on March 21, 2021.

Field of Invention

The present invention relates to a *p*-type transparent conductor and, more particularly to a *p*-type transparent conductor with deposition of the large area of highly reduced graphene oxide thin film by pulsed laser deposition method.

Background of the Invention

Over the past few years, there has been a massive growth of interest in research and industrial application for transparent conductors. A transparent conducting film is a transparent thin-film yet electrically conductive. Transparent conductors are manufactured to have surface conductivity while maintaining reasonable optical transparency. This unique class of surface conducting transparent conductive electrodes are used in a variety of applications, including optoelectronic devices, such as photovoltaic (PV) or solar cells, antistatic films, gas sensors, organic light-emitting diodes, organic photo-detectors, liquid crystal and high definition displays, electroluminescent devices, electromagnetic wave shielding layers and smart windows, as well as architectural coatings where high transparency and conductivity are required. For use in these applications, the electrode materials must exhibit both exceptional high optical transmittance and low sheet resistance (or high electrical conductivity). Such transparent electrical conductors are applied to such optoelectronic devices in the form of a coating and are widely known as transparent conductive coating (TCC) or transparent conductive oxides (TCO) materials.

More commonly used transparent and conductive oxides (TCO) include metal oxides, such as indium tin oxide (ITO), which are the industry standard materials to provide optical transparency and electrical conductivity. ITO is the dominant transparent conductor, providing the best-known combination of transparency (80%) and sheet resistance (10Ω/□). However, metal oxide films are fragile and prone to damage during bending or other physical stresses. ITO is increasingly expensive due to the scarcity of indium. ITO has limited environmental chemical stability and is unstable in the presence of an acid or base. Their finite permeability can lead to device degradation and they are prone to predisposition to ion diffusion from ionic conductive layers. ITO is not flexible and their use in flexible displays, solar cells and touch panels are severely limited. There also may be issues with the adhesion of metal oxide films to substrates that are prone to adsorbing moisture and get separated from the surface. They also require elevated deposition temperatures and/or high annealing temperatures to achieve high conductivity levels. In addition, surface irregularities can cause problematic sparking.

The possible replacements of ITO include metal grids, metallic nanowires, and carbon nanotubes (CNT), while none of them provides performance as good as ITO. Carbon nanotubes are used to form a thin film of highly porous mesh of electron-conducting paths on an optically transparent substrate, such as glass or polymer. However, there are several issues associated with the use of CNTs, namely, a higher CNT content leads to higher conductivity but lower transmittance; typical sheet resistances of CNT-based electrodes is 200-1,000 ohms/square (Ω/□) at an optical transmittance of 80-90% which is relatively high when compared to approximately 10-50 ohms/square of high-end ITO, which makes CNT electrodes far from being adequate for the practical applications in both current-based devices and voltage-driven devices. Metal nanowire-based conductive transparent films also suffer from the same problems as of carbon nanotubes. Although individual metal nanowires such as Ag nanowires have high electrical conductivity, the contact resistance between metal nanowires is significant. Additionally, Ag nanowire films are difficult to make a free-standing thin film of structural integrity coated on a substrate. In particular, Ag nanowire films deposited on a plastic substrate exhibit unsatisfactory flexibility, mechanical stability and the surface smoothness is also poor. All metal

nanowires still have a long-term stability issue, making them unacceptable for practical use. When metal nanowire films are exposed to air and water, nanowires get easily oxidized, leading to a sharp increase in sheet resistance and haze of the films. Conductive polymers have also been used as optically transparent electrical conductors. However, they generally have lower conductivity values and higher optical absorption at visible wavelengths compared to the metal oxide films and suffer from lack of chemical and long-term stability.

Accordingly, there remains a need in the art to provide transparent conductor oxides having desirable electrical, optical, and mechanical properties, namely good stability, high transparency, and excellent conductivity. In particular, it is desirable to provide a cost-efficient transparent conductive coating that is adaptable to any substrates, which demonstrates improved adhesion between the substrates and coatings, and can be manufactured in a low-cost and high-throughput process.

The search for new electrode materials with good stability, high transparency, and excellent conductivity has identified a more viable transparent conductive coating (TCC) based on carbon, specifically graphene. Graphene is a promising alternative to ITO; the term "graphene" usually refers to one or more atomic layers of graphite. Graphene is a two-dimensional plane of carbon atoms arranged in a hexagonal honeycomb structure. An isolated plane of carbon atoms organized in a hexagonal lattice is commonly referred to as a single-layer graphene sheet. Few-layer graphene refers to a stack of up to 5-10 planes of hexagonal carbon atoms bonded along the thickness direction. Graphene is highly transparent (97.3%) over wide wavelengths ranging from visible to near-infrared (IR). Good optical transparency and good electrical conductivity of graphene have motivated researchers to investigate graphene films for transparent and conductive electrode (TCE) applications. Graphene structures have been predicted and demonstrated to have many remarkable properties, such as high electron and hole mobilities with a symmetrical electron and hole band structure, high current-carrying capacity, high in-plane thermal conductivity, high tensile strength, and high mechanical stability. Owing to its covalent carbon-carbon bonding, graphene is also one of the stiffest materials with a remarkably high Young's modulus of ~1 TPa, yet stretchable and bendable at the same time, with a

maximum stretchability of up 20%. The combination of its high transparency, wide-band optical tunability, and excellent mechanical properties make graphene a very promising candidate for flexible electronics, optoelectronics, and photonics. The technical breakthrough of large-scale graphene synthesis has further accelerated the employment of graphene films as transparent electrodes. Graphene sheets, accordingly, show great potential as another material option for electronic applications.

However, in utilizing graphene as transparent electrodes in optoelectronic devices, the key challenge is to reduce the sheet resistance values, which provides the best-known combination of transparency (90%) and sheet resistance (<100Ω/□). To achieve ultralow sheet resistance, the typical prior art approach is by heavily doping graphene. Currently, chemical doping has been shown to effectively reduce the sheet resistance of graphene. However, doping is known to reduce the transmittance of the material for several reasons. First, the optical absorption of free carriers increases with the increasing concentration of carriers. Second doping is known to change the density of states function; this increase in absorption as a function of the doping level causes a fundamental trade-off between electrical conductivity and transmittance in TCO. Sn-doped In_2O_3 is considered a potential *n*-type TCO since it has a high electrical conductivity of the order of 10^4 S/cm, transmittance above 80 % in the visible range. Even though the first *p*-type TCO ($CuAlO_2$) was reported in 1997, a promising counterpart for *n*-type TCO is still elusive in terms of high optical transparency and electrical conductivity due to the strong localization of the holes in the O_{2p} orbitals. Moreover, recent developments in photovoltaics have further accelerated the demand for the investigation of suitable *p*-type transparent electrodes.

Though single- and few-layer graphene offer such significant advantages, the current methods for achieving single- and few-layer graphene are very limited. Existing methods include high-temperature vacuum annealing of SiC single-crystal substrates, hydrocarbon decomposition on single-crystal metal substrates under ultra-high vacuum (UHV) conditions, or manually cleaving highly oriented pyrolytic graphite (HOPG) using adhesive tape on SiO_2 substrates. These methods are not well suited for large-scale manufacturing. Conventional methods of forming transparent conductive coatings on transparent substrates include dry and wet processes. In dry processes, plasma vapor

deposition (PVD) (including sputtering, ion plating, and vacuum deposition) or chemical vapor deposition (CVD) is used to form a conductive transparent film of a metal oxide. The films produced using dry processes have both good transparency and good conductivity. However, these films, particularly ITO, are expensive and require complicated apparatuses that result in poor productivity. Other problems with dry processes include difficult application results when trying to apply these materials to continuous and/or large substrates. In conventional wet processes, conductive coatings are formed using electrically conductive powders mixed with liquid additives. In all of these conventional methods using metal oxides and mixed oxides, the materials suffer from supply restriction, lack of spectral uniformity, poor adhesion to substrates, and brittleness. In addition, vacuum deposition is a costly process and requires specialized equipment.

In a graphene film made by metal-catalyzed chemical vapor deposition (CVD), each graphene plane loses 2.3-2.7% of the optical transmittance and, hence, a five-layer graphene sheet or a film with five single-layer graphene sheets stacked together along the thickness direction would likely have optical transmittance lower than 90%.

Therefore, strong and urgent needs exist for more reliable processes and/or *p*-type TCE materials that exhibit outstanding performance. It also desirable to provide methods for fabricating such transparent conductors that do not require expensive or complicated systems.

US patent 908252 discloses a transparent conductor comprising of: a graphene layer and a permanent dipole layer on the graphene layer configured to electrostatically dope the graphene layer, wherein the permanent dipole layer being polarised and which maintains its dipole orientations without any applied electric field, wherein the permanent dipole layer is formed from a material comprising at least one of polar molecules or ions, and wherein the dipoles of the material are aligned to create the polarised permanent dipole layer.

US Patent application 20100021708 provides a large-area single- and few-layer graphene on arbitrary substrates, where a film of single-layer to few-layer graphene is formed by

depositing a graphene film via chemical vapor deposition on a surface of a growth substrate. The surface on which the graphene is deposited can be a polycrystalline nickel film, which is deposited by evaporation on a SiO_2/Si substrate. A protective support layer is then coated on the graphene film to provide support for the graphene film and to maintain its integrity when it is removed from the growth substrate. The surface of the growth substrate is then etched to release the graphene film, and the protective support layer from the growth substrate, wherein the protective support layer maintains the integrity of the graphene film during and after its release from the growth substrate. After being released from the growth substrate, the graphene film and protective support layer can be applied to an arbitrary target substrate for evaluation or use in any of a wide variety of applications.

Another US Patent 6103604 relates to a transparent electrical conductor that provides relatively high electrical conductivity and transmittance in the visible/near-infrared (VNIR), relative to known transparent electrical conductors, such as tin-doped indium oxide (ITO). The transparent electrical conductor is formed from a plurality of quantum wells formed between the interfaces of three layers of lattice-matched, wide bandgap materials, such as AlGaN and GaN. A material with a bandgap much larger than known materials used for such transparent electrical conductors, such as ITO, is selected. Both embodiments of the invention may be formed on a transparent substrate and provide relatively better transmittance in the VNIR at sheet electrical resistances of four or fewer ohms/square than known materials, such as tin-doped indium oxide (ITO).

Russian patent 2567949 relates to a technique for large area deposition of thin graphene films, which can be doped, for use thereof as a transparent conductive coating. An intermediate doped thin graphene film is hetero-epitaxially grown on a catalyst thin film with a single-orientation large-grain crystal structure, placed on a target receiving substrate, which includes solid-state dopants which are incorporated therein by a fusion process, followed by doping the intermediate thin graphene film with n-type or p-type dopants to facilitate the migration of the solid-state dopants from the target receiving substrate into the intermediate thin graphene film via thermal diffusion. Once formed,

the thin graphene films can be separated from the carrier substrates and transferred to receiving substrates, for example, for incorporation into an intermediate or finished product.

US Patent 8871296 provides a method of producing a transparent and conductive film, comprising (a) forming aerosol droplets of a first dispersion comprising a first conducting nano filaments in a first liquid; (b) forming aerosol droplets of a second dispersion comprising a graphene material in a second liquid; (c) depositing the aerosol droplets of a first dispersion and the aerosol droplets of a second dispersion onto a supporting substrate; and (d) removing the first liquid and the second liquid from the droplets to form the film, which is composed of the first conducting nano filaments and the graphene material having a nano filament-to-graphene weight ratio of from 1/99 to 99/1, wherein the film exhibits an optical transparency no less than 80% and sheet resistance no higher than 300 ohm/square.

In view of the above-said background and prior-art, there still exists a need in the art for a *p*-type transparent conductor with an optimal combination of higher transmittance and reduced sheet resistance. Further, there is also a need for a technique for large-scale deposition of graphene films onto the substrate, which is less expensive and more efficient.

The present invention provides a *p*-type transparent conductor with a highly reduced graphene oxide. In particular, it provides a direct growth of large-area reduced graphene oxide thin films using pulsed laser deposition (PLD). The direct growth of wafer-scale highly reduced graphene oxide thin films of the present invention shows physical and chemical characteristics similar to chemically grown reduced graphene oxide. The present invention outperforms the chemically grown reduced graphene oxide in their performance as *p*-type transparent conductors. The direct growth of wafer-scale highly reduced graphene oxide thin films of the present invention has higher sp^2 contents leading to the reduction of resistivity (and sheet resistance) of the film and also shows very high transmittance value. The highly reduced graphene oxide thin films of the present invention have high Figures of Merit in the family of *p*-type transparent conductors, making them important for their applications as transparent conductors.

Furthermore, other desirable features and characteristics of the present invention will become apparent from the subsequent detailed description of the invention and the appended claims, taken in conjunction with the accompanying drawings and this background of the invention.

Objects of the Invention:

The main object of the present invention is to provide a *p*-type transparent conductor with deposition of a large area of highly reduced graphene oxide thin film by pulsed laser deposition method.

The primary object of the present invention to provide a direct growth of large-area wafer-scale reduced graphene oxide thin films using control of the growth ambient of pulsed laser deposition (PLD).

It is another object of the present invention to provide pulsed laser deposition grown reduced graphene oxide thin films showing physical and chemical characteristics similar to chemically grown reduced graphene oxide. Still, another object of the present invention is to provide highly reduced graphene oxide thin films that outperform the chemically grown reduced graphene oxide in their performance as *p*-type transparent conductors.

It is another object of the present invention is to provide wafer-scale reduced graphene oxide thin films having higher sp^2 contents leading to the reduction of resistivity or sheet resistance of the film.

It is another object of the present invention is to provide highly reduced graphene oxide thin films having very high transmittance value, eligible for setting a new standard in transparent coating oxide films.

Although the present invention is mainly designed as a promising *p*-type transparent conductor with deposition of a large area of highly reduced graphene oxide thin film by pulsed laser deposition method, it goes without saying that the present invention can be

applied and adapted to different transparent conductors films and their applications as transparent conductors.

Summary of the Invention

The present invention provides a *p*-type transparent conductor with deposition of large area of highly reduced graphene oxide thin film by pulsed laser deposition method. The present invention provides a *p*-type transparent conductor with highly reduced graphene oxide thin film, comprising of: a substrate; and a highly reduced graphene oxide thin film deposited on the said substrate, wherein said reduced graphene oxide thin film is directly grown on the substrate by pulsed laser deposition in a reduced atmosphere. Wherein said deposition is a large area deposition of reduced graphene oxide thin films using pulsed laser deposition. The highly reduced graphene oxide thin films are directly obtained by pulsed laser deposition growth in a reducing atmosphere that helps in reducing the contribution of oxygen-containing functional groups in the grown film leading to the formation of more sp^2 carbon system, thereby enabling the reduction of resistivity or sheet resistance of the film. The highly reduced graphene oxide thin film of the present invention shows a high transmittance value of ~98% at 550 nm and electrical conductivity of ~ 7000 S/m ($\rho \sim 0.014\ \Omega$-cm). This shows that the highly reduced graphene oxide thin film having a very high transmittance value while maintaining the good electrical conductivity of the grown film eligible for setting a new standard in transparent coating oxide films.

An embodiment of the present invention provides a method of synthesis of *p*-type transparent conductor with reduced graphene oxide thin films, comprising steps of: Selecting a suitable substrate onto which the transparent coating of reduced graphene oxide thin film is to be coated; Maintaining the substrate in the desired temperature range; Maintaining the base pressure of the deposition chamber at a pre-determined pressure level prior to growth; Maintaining the desired substrate temperature in the deposition chamber; Depositing highly reduced graphene oxide thin film directly on to the said substrate by pulsed laser deposition technique in a reducing atmosphere; Rotating the substrate throughout the deposition process thereby enabling uniform deposition of highly

reduced graphene oxide thin film on the substrate; Maintaining the deposition chamber under reducing atmosphere throughout the process, which efficiently reduces the oxygenated carbon films to improve the electronic quality achieving graphene-like films.

The present invention provides a pulsed laser deposition technique for the wafer-scale growth of highly reduced graphene oxide film with exceptional film quality. This clean approach for synthesizing ultra-smooth stable thin films at a lower process temperature is easily scaled to a large area wafer-scale integration. Due to growth in the reducing atmosphere, the reduced graphene oxide thin film of the present invention has very high transmittance while maintaining good electrical conductivity. The grown films show a *p*-type conductivity with a high FoM, allowing rapid integration with existing technologies that require solutions for transparent conductors.

Other features and advantages of embodiments will be apparent from the accompanying drawings and from the detailed description that follows.

Brief Description of the Drawings

Fig.1(a) represents an AFM image of the highly reduced graphene oxide thin film grown on SiO_2/Si substrate for evaluating the thickness of the film.

Fig.1(b) represents the corresponding height profile of the highly reduced graphene oxide thin film grown on SiO_2/Si substrate showing the thickness of the film as 4.82 nm.

Fig.1(c) represents the highly reduced graphene oxide thin film grown on SiO_2/Si substrate showing ultra-smooth morphology with an rms roughness of 0.45 nm.

Fig.2(a) represents the Raman intensity mapping in the region of 1100 cm^{-1} to 1800 cm^{-1} of the highly reduced graphene oxide thin film on SiO_2/Si substrate showing a uniform coverage of the film over the scanned area of 25 μm x 25 μm.

Fig.2(b) represents the XPS Survey scan of the highly reduced graphene oxide thin film having intense C1s band with respect O1s band with a C/O ratio of 18.3 showing a higher reduction of the grown film.

Fig.3(a) represents the UV-visible transmission spectrum of highly reduced graphene oxide thin film on a transparent fused silica substrate showing a very high transmittance value of ~98% at 550 nm.

Fig.3(b) represents the resistivity *vs.* temperature plot for the highly reduced graphene oxide thin film grown on SiO_2/Si substrate showing the semiconducting behavior.

Fig.4(a) represents the temperature-dependent Hall resistance plot, R_{xy} *vs.* B, showing a positive slope, confirming the *p*-type nature of the highly reduced graphene oxide thin film transparent conductor throughout the measured temperatures.

Fig.4(b) represents the figure of merit introduced by Hackle (FoM^H) and Gordon (FoM^G) (in units of $M\Omega^{-1}$) for evaluating the performance of *p*-type transparent films of the present invention (121) compared with the reported *p*-type transparent coating oxides (TCOs).

The performance of *p*-type transparent films of the present invention as seen in fig. 4b is compared with the following reported *p*-type transparent coating oxides (TCOs):

1. Juvaid, M.M., et al., Direct Growth of Waferscale, Transparent, p-Type Reduced Graphene Oxide Like Thin Films by Pulsed Laser Deposition. ACS Nano, 2020.

2. Joshi, U.S., et al., Combinatorial synthesis of Li-doped NiO thin films and their transparent conducting properties. Applied Surface Science, 2006. 252(7): p. 2524-2528.

3. Zhang, K.H.L., et al., Perovskite Sr-Doped LaCrO3 as a New p-Type Transparent Conducting Oxide. Advanced Materials, 2015. 27(35): p. 5191-5195.

4. Dekkers, M., G. Rijnders, and D.H.A. Blank, ZnIr2O4, a p-type transparent oxide semiconductor in the class of spinel zinc-d6-transition metal oxide. Applied Physics Letters, 2007. 90(2): p. 021903.

5.. Duan, N., et al., Transparent p-type conducting CuScO2+x films. Applied Physics Letters, 2000. 77(9): p. 1325-1326.

6. Kudo, A., et al., SrCu2O2: A p-type conductive oxide with wide band gap. Applied Physics Letters, 1998. 73(2): p. 220-222.

7. Bhatia, A., et al., High-Mobility Bismuth-based Transparent p-Type Oxide from High-Throughput Material Screening. Chemistry of Materials, 2016. 28(1): p. 30-34.

8. Arca, E., K. Fleischer, and I.V. Shvets, Magnesium, nitrogen codoped Cr2O3: A p-type transparent conducting oxide. Applied Physics Letters, 2011. 99(11): p. 111910.

9. Yanagi, H., et al., Electronic structure and optoelectronic properties of transparent p-type conducting CuAlO2. Journal of Applied Physics, 2000. 88(7): p. 4159-4163.

While the invention is amenable to various modifications and alternative forms, specifics thereof have been shown by way of example in the drawings and will be described in detail. It should be understood, however, that the intention is not to limit the invention to the particular embodiments described. On the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the accompanying drawings. Prior to this, terms and words used in the present specification and claims should not be construed as limited to ordinary or dictionary terms, and the inventor should appropriately interpret the concept of the term appropriately to describe its own invention in the best way. The present invention should be construed as meaning and concept consistent with the technical idea of the present invention based on the principle that it can be defined. Therefore, the embodiments described in this specification and the configurations shown in the drawings are only the most preferred embodiments of the present invention and do not represent all the technical ideas of the present invention. Therefore, it should be understood that equivalents and modifications are possible.

Detailed Description of the Invention with Respect to the Drawings

The present invention as embodied by the *p*-type transparent conductor with reduced graphene oxide thin films and one-step synthesis thereof," succinctly fulfills the above-

mentioned need(s) in the art. The present invention has objective(s) arising as a result of the above-mentioned need(s), said objective(s) being enumerated below. In as much as the objective(s) of the present invention are enumerated, it will be obvious to a person skilled in the art that, the enumerated objective(s) are not exhaustive of the present invention in its entirety, and are enclosed solely for the purpose of illustration. Further, the present invention encloses within its scope and purview, any structural alternative(s) and/or any functional equivalent(s) even though, such structural alternative(s) and/or any functional equivalent(s) are not mentioned explicitly herein or elsewhere, in the present disclosure. The present invention therefore encompasses also, any improvisation(s)/ modification(s) applied to the structural alternative(s)/functional alternative(s) within its scope and purview. The present invention may be embodied in other specific form(s) without departing from the spirit or essential attributes thereof.

Throughout this specification, the use of the word "comprise" and variations such as "comprises" and "comprising" may imply the inclusion of an element or elements not specifically recited.

The present invention provides a *p*-type transparent conductor with highly reduced graphene oxide thin film, comprising of : a substrate; and a highly reduced graphene oxide thin film deposited on the said substrate, wherein said reduced graphene oxide thin film is directly grown on the substrate by pulsed laser deposition in a reduced atmosphere.

In the preferred embodiment of the present invention, wherein said substrate is selected from a group consisting of, SiO_2/Si, fused silica and/or combination thereof.

In the preferred embodiment of the present invention, wherein said deposition is a large area deposition of reduced graphene oxide thin films using pulsed laser deposition.

Pulsed laser deposition (PLD) is a powerful tool for growing large-area thin films with high uniformity and surface smoothness. Pulsed laser deposition growth of high-quality wafer-scale rGO-like films deposited in an argon and oxygen environment is demonstrated prior-art. A major challenge in this growth is precise optimization of the oxygen-containing functional groups of graphene, which engineers their physical

properties. In contrast to the strong chemical reducing agents involved in the conventional chemical methods, the pulsed laser deposition process involves lesser control parameters (varying oxygen partial pressures and growth temperature ~680 ^{0}C) that help to tune the composition of the oxygen-containing functional groups in an easily reproducible manner. Generally, to further reduce the oxygen content from grapheme oxide films and to improve the electrical conductivity, the films are annealed in a reducing atmosphere.

In the preferred embodiment of the present invention, highly reduced graphene oxide thin films are directly obtained by pulsed laser deposition growth in a reducing atmosphere that helps in reducing the contribution of oxygen-containing functional groups in the grown film leading to the formation of more sp^2 carbon system.

In the preferred embodiment of the present invention, wherein the reduced atmosphere is a selected from a group of inert gases, including argon, hydrogen and/ or combination thereof.

In an embodiment of the present invention, direct growth of large-area wafer-scale highly reduced graphene oxide thin films is synthesized using the one-step pulsed laser deposition process.

In the embodiment of the present invention, wherein said direct growth of large-area wafer-scale measures at least 4- inch diameter.

In the preferred embodiment of the present invention, wherein said substrate is selected from SiO_2/Si, fused silica and/or combination thereof.

During the pulsed laser deposition in a reducing atmosphere, some of the sp^2 conjugated domains remain intact, while the oxygen moieties significantly reduce and lead to more sp^2 hybridized carbon. A dense glassy carbon target was ablated by a 266 nm PowerLite 8010 Nd: YAG laser with 500 laser shots (10 Hz repetition rate, fluence of 2.9 J/cm^2) by beam scanning mode of PLD, where the UV laser beam was scanned while ablating the glassy carbon target.

In an embodiment of the present invention, the thickness of the highly reduced graphene oxide thin film deposited on the substrate is detected using the AFM morphology image of the highly reduced graphene oxide thin film grown on the substrate taken at the edge of a Hall bar channel.

Figure 1(a) shows the image of a highly reduced graphene oxide thin film on a 4-inch fused silica wafer. Figure 1(b) represents the AFM morphology of highly reduced graphene oxide thin films grown on SiO_2/Si substrate, where the image is taken at the edge of a Hall bar channel enabling the detection of the thickness of the reduced graphene oxide thin film. Figure 1(c) provides the corresponding thickness line profile, which shows a thickness of 4.8 nm for film synthesized by 500 laser pulses. Figure 1(d) shows the highly reduced graphene oxide thin film of the present invention having an ultra-smooth surface morphology and exhibiting rms roughness of ~ 0.45 nm.

In an embodiment of the present invention, uniform coverage of the highly reduced graphene oxide thin film deposited on the substrate is detected using Raman Intensity mapping acquired in both D and G bands. Whereas the chemical states of the graphene oxide thin film is investigated using the XPS spectrum.

Figure 2(a) Raman Intensity mapping of the highly reduced graphene oxide thin films over 25 μm x 25 μm area in the region of 1100 cm^{-1} to 1800 cm^{-1} of the film on SiO_2/Si substrate showing uniform coverage of the highly reduced graphene oxide film over the scanned area. The said Raman mapping was acquired for both D and G bands in the spectral window of 1000 cm^{-1} to 1800 cm^{-1}. The chemical states of the graphene oxide thin film were investigated by the XPS spectrum. The survey scan of the XPS spectrum of the highly reduced graphene oxide thin film is shown in Figure 2(b). The intense C1s band with a lower O1s band having a high C/O ratio of 18.3, indicates the formation of highly reduced graphene oxide film in a reduced Ar/H_2 atmosphere.

In the preferred embodiment of the present invention, wherein said highly reduced graphene oxide thin film shows transmittance value of ~98% at 550 nm.

In the preferred embodiment of the present invention, wherein said highly reduced graphene oxide thin film shows an electrical conductivity of ~ 7000 S/m (ρ ~ 0 .014 Ω-cm).

In the preferred embodiment of the present invention, wherein said highly reduced graphene oxide thin film having a very high transmittance value while maintaining good electrical conductivity of the grown film.

Figure 3(a) shows the optical transmittance of the highly reduced graphene oxide thin film grown on a transparent fused silica substrate in an Ar/H_2 atmosphere. A transmittance value of ~98% is obtained at 550 nm, and the transmittance spectrum lies well above 90% throughout the visible region. Figure 3(b) shows resistivity *vs.* temperature curve for a highly reduced graphene oxide thin film grown on a SiO_2/Si substrate *via* PLD and showing the semiconducting behavior. The Hall bar device geometry used for the transport measurements is shown in the inset of Figure 3(b).

Reduced graphene oxide thin film has been reported to be a *p*-type semiconductor due to the presence of oxygen-containing functional groups that act as electron-withdrawing groups. The *p*-type conductor conduction of reduced graphene oxide thin film is confirmed through a temperature-dependent Hall measurement.

In the preferred embodiment of the present invention, Hall measurement was performed on the patterned film grown on the SiO_2/Si substrate, which identifies the nature of the carriers in the highly reduced graphene oxide thin film as shown in Figure 5(a), where the slope of Rxy *vs.* B is positive.

To assess the performance of *p*-type Transparent conducting film, Haacke proposed a figure of merit (FoM) formalism in which the transmittance (T) and sheet resistance (Rs) is correlated by the following relation.

$$FoM^H = \frac{T^{10}}{R_S} \text{ (in units of M } \Omega^{-1})$$

Since the above evaluation overestimates the importance of optical transparency, an improved FoM was introduced by Gordon, which correlates the electrical conductivity (σ) and the visible absorption coefficient(α), with a zero reflectance (R= 0) approximation FoM^G can be written as;

$$FoM^G = \frac{\sigma}{\alpha} \approx \frac{-1}{R_S \ln T} \text{ (in units of M } \Omega^{-1})$$

FoM^G is strongly dependent on the value of sheet resistance rather than the value of transmittance.

In the preferred embodiment of the present invention, the *p*-type transparent conductor performance of the reduced graphene oxide thin film were measured based on the above two approaches exhibits FoMs 27 MΩ^{-1} and 1679 MΩ$^{-1,}$ respectively. Figure 4(b) shows their comparison with the existing *p*-type transparent conducting films. This indicates that the highly reduced graphene oxide thin film of the present invention, which although are ultrathin with a thickness of <5 nm, has a higher performance among other *p*-type transparent conducting films.

The present invention provides a pulsed laser deposition technique for the wafer-scale growth of highly reduced graphene oxide film with exceptional film quality. This clean approach for synthesizing ultra-smooth stable thin films at a lower process temperature (~680 ^{0}C), as compared to conventional chemical routes can be easily scaled to a large area wafer-scale integration. Due to growth in the reducing atmosphere, reduced graphene oxide thin film of the present invention has very high transmittance (~98% at 550 nm) while maintaining good electrical conductivity (~7000 S/m). The grown films show a *p*-type conductivity with a high FoM even for a film having thickness ~5 nm, which is a significant advancement as compared to previous reports and would allow rapid integration with existing technologies that require solutions for transparent conductors.

In an embodiment of the present invention, method of synthesis of *p*-type transparent conductor with reduced graphene oxide thin films, comprises steps of :

a) Selecting a suitable substrate onto which the transparent coating of reduced graphene oxide thin film is to be coated, Where said substrate is selected from a group of SiO_2/Si, fused silica and or combination thereof;
b) Maintaining the substrate in the desired temperature of 680 ^{0}C;
c) Maintaining the base pressure of the deposition chamber at a pre-determined pressure level prior to growth;
d) Depositing highly reduced graphene oxide thin film directly onto the said substrate by pulsed laser deposition technique in a reducing atmosphere.
e) Rotating the substrate throughout the deposition process thereby enabling uniform deposition of highly reduced graphene oxide thin film on the substrate;
f) Maintaining the deposition chamber under reducing atmosphere throughout the direct growth of highly reduced graphene oxide thin film onto the said substrate and efficiently reduces the oxygenated carbon films to improve the electronic quality achieving graphene-like films.

Example 1

The present invention provides a *p*-type transparent conductor with highly reduced graphene oxide thin film, comprising of: a substrate; and a highly reduced graphene oxide thin film deposited on the said substrate, wherein said reduced graphene oxide thin film is directly grown on the substrate. The deposition of reduced graphene oxide thin film is on a large area performed by pulsed laser deposition technique in a reducing atmosphere. Wherein said substrate selected is SiO_2/Si and fused silica. The substrate is maintained at the desired temperature of 680 ^{0}C at a base pressure of 6 x 10^{-6} Torr prior to growth. Inside the deposition chamber, deposition of highly reduced graphene oxide thin film is performed directly on to the said substrate by pulsed laser deposition technique in a reducing atmosphere. Substrate is rotated throughout the deposition process to ensure uniform coverage. During growth, reducing atmosphere with a mixture of 95% Ar + 5% H_2 gas is maintained at a pressure of 20.0 mTorr in the deposition chamber. Growth in the Hydrogen atmosphere is known to assist in the efficient reduction of oxygenated carbon

films to improve their electronic quality to achieve graphene-like films. The highly reduced graphene oxide thin film of the present invention exhibits a transmittance value of ~98% at 550 nm and electrical conductivity of ~ 7000 S/m (ρ ~ 0 .014 Ω-cm). The thickness of the highly reduced graphene oxide thin film deposited on the substrate is detected using the AFM morphology image of the highly reduced graphene oxide thin film grown on the substrate taken at the edge of a Hall bar channel. Uniform coverage of the highly reduced graphene oxide thin film deposited on the substrate is detected using Raman Intensity mapping acquired in both D and G bands. Whereas the chemical states of the graphene oxide thin film is investigated using the XPS spectrum. Performance of the reduced graphene oxide thin film measured based on the two approaches, namely Haacke formalism and Gordon formalism, exhibits FoMs values of 27 $M\Omega^{-1}$ and 1679 $M\Omega^{-1}$, respectively. The highly reduced graphene oxide thin films of the present invention have high figures of merit in the family of *p*-type transparent conductors films, making them important for their applications as transparent conductors.

It will be apparent to a person skilled in the art that the above description is for illustrative purposes only and should not be considered as limiting. Various modifications, additions, alterations, and improvements without deviating from the scope of the invention may be made by a person skilled in the art.

We claim,

1. A *p*-type transparent conductor with a highly reduced graphene oxide thin film, comprising of:

   a substrate; and

   a highly reduced graphene oxide thin film deposited on the said substrate,

   wherein said reduced graphene oxide thin film is directly grown on the substrate by pulsed laser deposition in a reduced atmosphere.

2. The *p*-type transparent conductor, as claimed in claim 1, wherein said substrate is selected from a group consisting of, SiO_2/Si, fused silica and/or combination thereof.

3. The *p*-type transparent conductor, as claimed in claim 1, wherein said deposition is a large area deposition of reduced graphene oxide thin films using pulsed laser deposition.

4. The *p*-type transparent conductor, as claimed in claim 1, highly reduced graphene oxide thin film is directly obtained by pulsed laser deposition growth in a reducing atmosphere, which enables reduction in the contribution of oxygen-containing functional groups in the grown film leading to the formation of more sp^2 carbon system.

5. The *p*-type transparent conductor, as claimed in claim 1, wherein the reduced atmosphere is selected from a group of inert gases including argon, hydrogen and/ or combination thereof.

6. The *p*-type transparent conductor, as claimed in claim 1, is synthesized by direct growth of large-area wafer-scale highly reduced graphene oxide thin films in a single step pulsed laser deposition process.

7. The *p*-type transparent conductor, as claimed in claim 1, wherein said direct growth of large-area wafer-scale measures at least 4- inch diameter.

8. The *p*-type transparent conductor, as claimed in claim 1, wherein said highly reduced graphene oxide thin film exhibits a transmittance value of ~98% at 550 nm.

9. The *p*-type transparent conductor, as claimed in claim 1, wherein said highly reduced graphene oxide thin film exhibits an electrical conductivity of ~ 7000 S/m ($\rho \sim 0.014\ \Omega$-cm).

10. A method of synthesis of *p*-type transparent conductor with reduced graphene oxide thin films comprises steps of :

a) Selecting a suitable substrate onto which the transparent coating of reduced graphene oxide thin film is to be coated, Where the said substrate is selected from a group of SiO_2/Si, fused silica and or combination thereof;
b) Maintaining the substrate in the desired temperature range of 680 ^{0}C;
c) Maintaining the base pressure of the deposition chamber at a pre-determined pressure level prior to growth;
d) Depositing highly reduced graphene oxide thin film directly onto the said substrate by pulsed laser deposition technique in a reducing atmosphere.
e) Rotating the substrate throughout the deposition process thereby enabling uniform deposition of highly reduced graphene oxide thin film on the substrate;
f) Maintaining the deposition chamber under reducing atmosphere throughout the direct growth of highly reduced graphene oxide thin film onto the said substrate to efficiently reduce the oxygenated carbon films to improve the electronic quality achieving graphene-like films.

11. The method of synthesis of *p*-type transparent conductor, as claimed in claim 10, wherein said process temperature is maintained at 680 ^{0}C.

12. The method of synthesis of *p*-type transparent conductor, as claimed in claim 10, wherein said base pressure of the deposition chamber is maintained at a base pressure of 6×10^{-6} Torr prior to growth.

13. The method of synthesis of *p*-type transparent conductor, as claimed in claim 10, wherein said reduced atmosphere inside the deposition chamber is a mixture of 95% Ar + 5% H_2 gas and maintained at a pressure of 20.0 mTorr in the deposition chamber.

14. The *p*-type transparent conductor, as claimed in claim 1, wherein the thickness of the highly reduced graphene oxide thin film deposited on the substrate is detected using the AFM morphology image of the highly reduced graphene oxide thin film grown on the substrate taken at the edge of a Hall bar channel.

15. The *p*-type transparent conductor, as claimed in claim 1, coverage of the highly reduced graphene oxide thin film deposited on the substrate is detected using Raman Intensity mapping.

16. The *p*-type transparent conductor, as claimed in claim 1, Chemical states of the highly reduced graphene oxide thin film is investigated using the XPS spectrum.

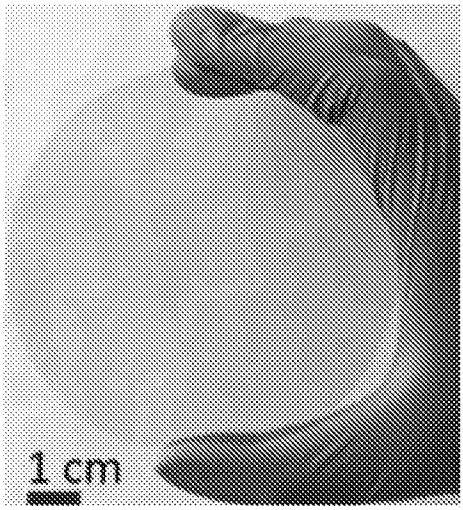


Figure 1a

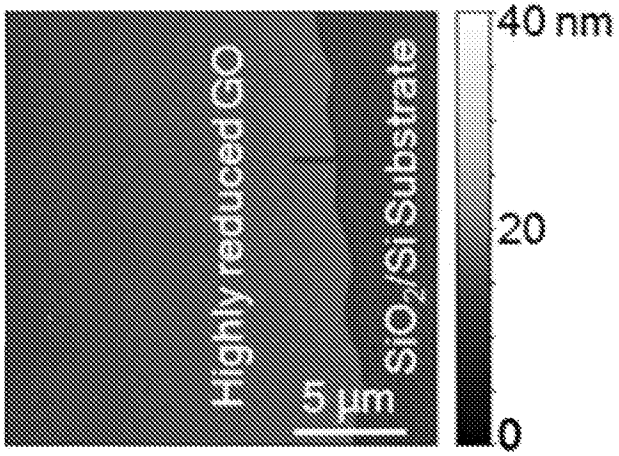


Figure 1b

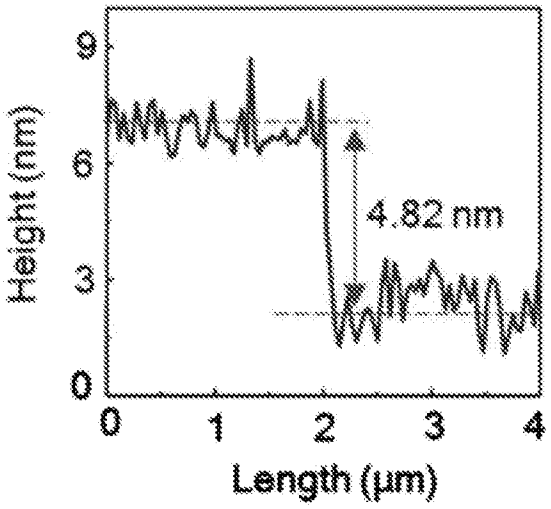


Figure 1c

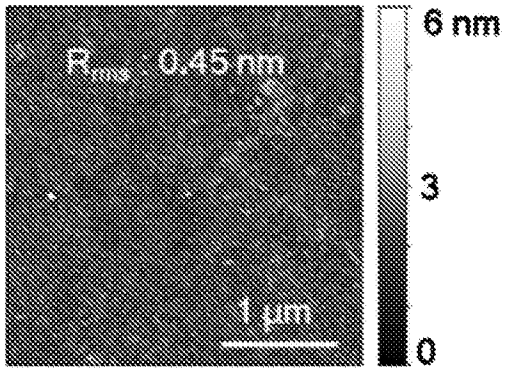


Figure 1d

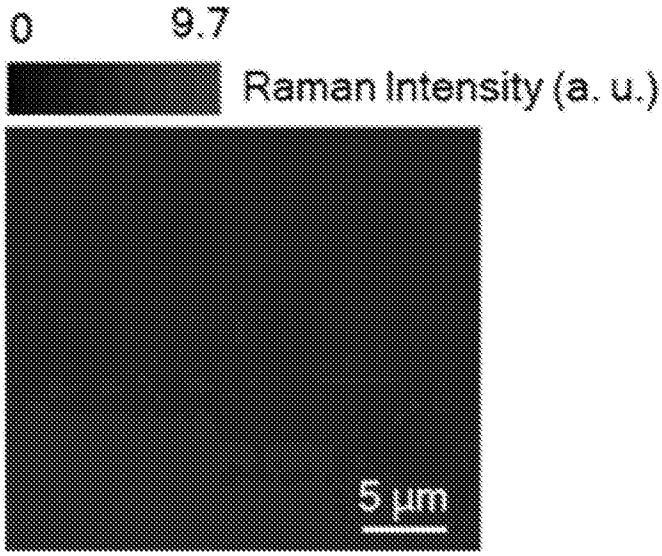


Figure 2a

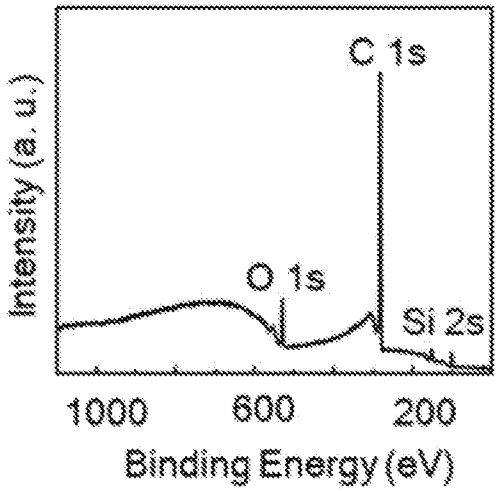


Figure 2b

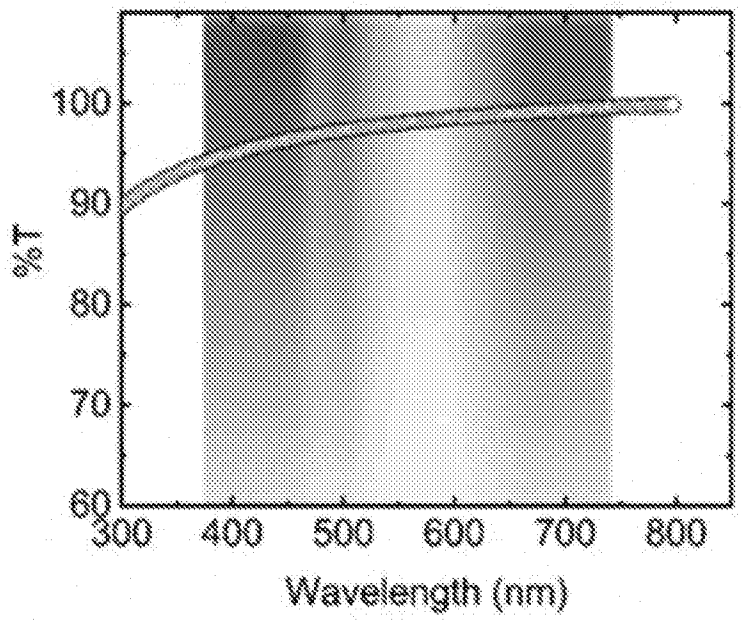


Figure 3a

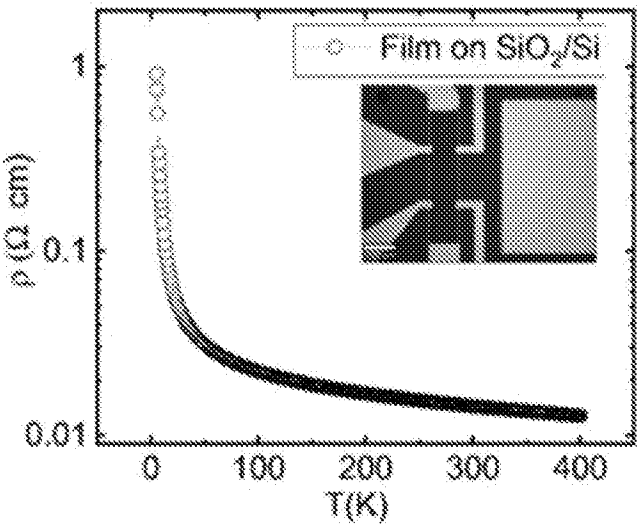


Figure 3b

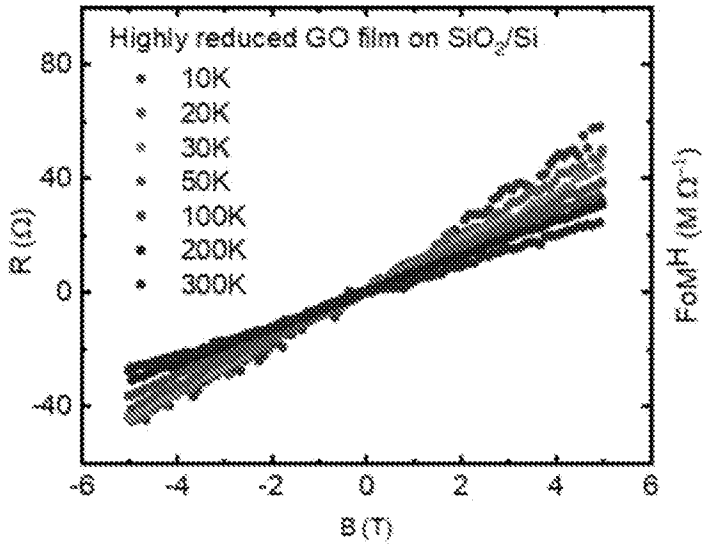


Figure 4a

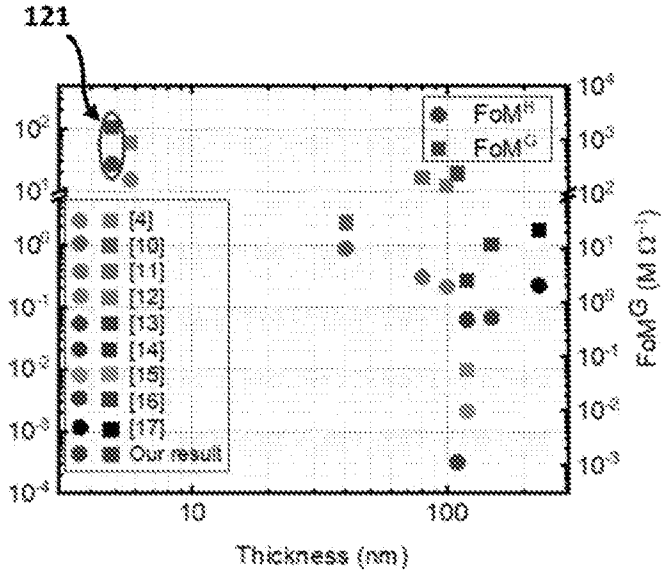


Figure 4b

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2022/050267

A. CLASSIFICATION OF SUBJECT MATTER
H01L33/42,H01L31/00 Version=2022.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DATABASES:- IPO INTERNAL DATABASE,PATSEER, GOOGLE SCHOLAR
KEYWORDS:- GRAPHENE OXIDE, CONDUCTOR, ATMOSPHERE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US20160332885A1 (Uchicago Argonne, LLC) (17-NOV-2016) (17-11-2016) Claims 1,13; Abstract	1-16
Y	Direct Growth of Wafer-Scale, Transparent, p-Type Reduced-Graphene-Oxide-like Thin Films by Pulsed Laser Deposition (M. M. Juvaid et al.) (26-FEB-2020)(26-02-2020) Full description	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16-06-2022	16-06-2022
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Surajit Das Telephone No. +91-1125300200