Graphene Research and Advances

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Introduction

SIO Grafen's Research Intelligence Report Series, published twice a year, aims to highlight some of the most interesting research findings on graphene and other two-dimensional (2D) materials that have emerged during the last few months.

High quality single layer graphene can be used for electronics and sensors applications, and a new technique has been developed for wafer-scale fabrication of high quality graphene devices. A careful statistical analysis revealed the crucial role of the graphene transfer and a separate report on the transfer is also discussed. A new strategy to functionalized and patterned graphene enabled the creation of thermoresponsive self-folding graphene shapes.

Printed electronics is an interesting area which could allow for new wearable technology to be realised. Graphene is an optimal material to be used in the field, due to its flexibility and conductivity. Different perspectives and applications are discussed here, such as ink-jet printing of graphene on textiles and on flexible substrates.

The electrons move significantly faster in graphene than in most semiconductors used today, which opens up the possibility to create devices working in the Teraherz (THz) range (that is 100-1000 times faster than the common Gigahertz technology). An example where graphene has been used to develop a THz-sensor is highlighted.

Graphene can be used as a filler in many different kinds of composites. The most work has by far been done on polymer composites in order to improve the mechanical and/or electrical or thermal conductivities. The field is significantly broader and in this Research Intelligence Report, new results on concrete composites and on graphene in polymer composites for flame retardancy are highlighted. Interesting ideas using animals to create the composites are also discussed.

Graphene is projected to have an impact also in the area of Life Science. It could for example be used in several types of neural interfaces, in biological sensing and imaging and as a biocompatible scaffold for cell culture.

Content:

Manufacturing

Wafer-Scale Integration

A huge part of the development in the semiconductor industry has been to increase the performance by reducing the size of the components and thereby increasing the device density. However, the diversity of device functionality has become increasingly important in recent years. Thanks to its intrinsic multifunctionality, graphene could have a real impact toward this goal. Even though graphene devices are working on a laboratory scale, they have not yet been successfully integrated in an industrial wafer-scale process. The key for near and mid-term success for electronic and sensor applications is to develop wafer-scale graphene and graphene-based devices compatible with the existing CMOS[1] technology. In a recent article, researchers in Mikael Östling's team at the KTH Royal Institute of Technology, developed a wafer scalable and CMOS compatible fabrication technique for graphene devices using transferred CVD[2] graphene. A statistical analysis of over 4500 graphene field-effect transistors was performed, showing a yield of 75%. A careful analysis of the quality of the graphene channel, oxide and top gate using Raman scattering, scanning electron microscopy, contact resistance, mobility and Dirac point shift analysis over the entire wafer indicated compressive strain, which is created during the transfer, as the main culprit of device failure. These results not only show that it is possible to fabricate graphene devices on a wafer-scale in a process compatible with current semiconductor technology, but also show which part of the process that should be tackled next in order to increase the yield in future process development.

A. D. Smith *et al. IEEE Trans. Electron Devices* **64**, 3919 (2017)
A. D. Smith *et al. IEEE Trans. Electron Devices* **64**, 3927 (2017)

Optimizing CVD Graphene Transfer

Researchers at IMEC in Belgium recently investigated the factors influencing the transfer of CVD graphene in more details. The key role at the interfaces on both sides of the graphene layer has been identified. After the CVD growth of graphene on platinum, water is

[1] CMOS: Complementary metal-oxide-semiconductor. Current technology for producing integrated circuits.
[2] CVD: Chemical Vapor Deposition. This process has been discussed in detail in previous edition of the report.

intercalated at the interface enabling the releases of the graphene layer later in the process. The graphene surface is then pressed against a hydrophobic target substrate before the graphene is delaminated. The use of a hydrophobic substrate ensures good adhesion of the graphene to the target. This technique presents several advantages over conventional techniques: it is cost efficient since the metallic catalyst substrate can be reused and because the transfer does not require a polymer support, therefore the presence of residue is completely avoided.

K. Verguts *et al. ACS Appl. Mat. Interfaces* **9**, 37484 (2017)

Self-folding Graphene

Previous studies have focused on taking advantage of the different properties of folded and wrinkled graphene. Although several techniques are available, they, in general, offer only limited precision and tunability in the 3D geometries achieved and no self-folding in response to external environmental stimuli has been reported. An article from a team in the United States show a strategy to modify the surface of graphene to acquire a thermoresponsive property. The graphene is functionalized with polydopamine (a mussel-inspired bioadhesive) on one side, before patterning. Several closing shapes were produced: flowers, dumbbells and square boxes. Self-folding of the structures was triggered by increasing the temperature to 45°C. This process is reversible; the shapes are returning to their original unfolded state when the temperature is decreased to under 25°C. A number of applications can take advantage of this versatile technique, for example to encapsulate and deliver cells or other biologic drugs.

Weinan Xu *et al. Sci. Adv.* **3**, e1701084 (2017)

Coatings

Coating textiles

Factors influencing the conductivity of textile fibres coated with graphene were investigated in another recent study. The effect of fibre topography and chemical nature were evaluated. Several different materials (PP, PLA, PE and nylon), extrusion parameters and precursor materials (monolayer and few-layer graphene) were investigated. The coating was produced by electrostatic adhesion of graphene to the surface of the fibres. Graphene was successfully coated on all samples, where the highest conductivity was reached for fibres with smooth surfaces. It was found that a pre-treatment of ultraviolet ozone can improve the conductivity, but also often damages the fibres by making them more fragile. Cracks in the graphene films, which can severely deteriorate the conductivity, were not formed during bending of the fibres, but rather already in the coating process. The untreated fibres could withstand 1000 bending cycles with a bending radius of 5 mm without any significant change in resistance. The coating was found to be strong and durable and could be further protected by encapsulation with an insulating polymeric layer.

A. I. Neves *et al. Scientific Reports* **7**, 4250 (2017)

Membrane for desalination

The potential of using graphene to desalinate water was discussed in the previous edition of this Research Intelligence Report (no 1, 2017). A new study reports an alternative method to desalinate water using graphene. The new method is based on spray coating of graphene and graphene oxide (GO) onto polysulfone support membranes modified with polyvinyl alcohol (PVA). The PVA layer was crucial in order to improve the mechanical robustness of the membranes, which were able to withstand intense cross-flows. A combination of graphene and GO was found to be more resistant to chlorine than pure GO membranes, which is necessary to withstand cleaning procedures.

The membranes could reject 85 % of NaCl, which is lower than the previous study. It is not (yet) good enough to desalinate water for drinking purposes, but it is adequate for agriculture and it should be possible to produce the membranes at large scale and low cost. The membranes also had a rejection of 96 % for an anionic dye, which can be used to filter out pollutants from textile manufacturing.

A. Morelos-Gomez *et al. Nature Nanotechnology* **12**, 1083 (2017)

Energy

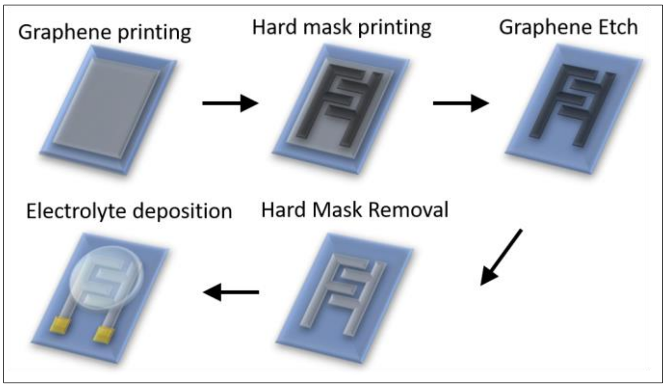
Personal Thermal Management

Wearables are ubiquitous and every year more and more functionalities are added to monitor and control our interaction with the environment. Among these, personal thermal management (PTM) has become more prevalent, bringing the potential of adjusting the body temperature via heating or cooling using wearable devices. Several technologies are available to perform one of these two functions, but none is so far able to achieve both warming and cooling in one textile. A recent article demonstrates that graphene paper is a promising material for wearable PTM. Graphene oxide gel is blade-coated on a sandpaper, allowing for easy release of thin films. The gel is dried, peeled and reduced. The obtained paper is electrically conducting, flexible and foldable, washable, possess a large area and has a good out-of-plane thermal conductivity. To warm up the body, the paper is heated using resistive (joule) heating from room temperature to body temperature using only 2.5V, a low value in comparison to the 12V needed for carbon nanotube based cloth, for example. Cooling of the body is ensured by passive cooling through the graphene paper, which is more efficient and much faster (the response time is also shortened from 150 to 7 s) than normal cotton fabric. This could be used as wearable personal cooling under medium temperature ranges. Together with the heating results, this confirms the great potential of graphene paper for personal thermal management wearable devices.

Y. Guo *et al. Small* **13**, 1702645 (2017)

Flexible Micro-Supercapacitors

In a previous edition of the Research Intelligence Report (no 2, 2016), a study by researchers in Mikael Östling's team at the KTH Royal Institute of Technology demonstrated that it is possible to fabricate an all-solid-state micro-supercapacitor based on printed graphene electrodes and drop-cast polymer electrolyte. Previously, they reported devices with capacitance of about 0.1 mF/cm^2 and life cycle of over 1000 times, performances comparable to other graphene-based micro-supercapacitor. However, these devices had a non-uniform thickness due to the fact that when ink dries, the perimeter of the printed area ends up with a higher density/thickness of flakes than the centre of the printed area (the "coffee stain" effect). In a more recent study, the same team improved the fabrication technique and produced transparent and flexible micro-supercapacitors. The researchers developed a technique to uniformize the thickness of the entire useful area of printed graphene. First, a larger area than the desired one is printed. Then a hard mask of printed silver is used to define the desired graphene pattern by etching uncovered parts with O_2 plasma. The silver mask can then be removed, leaving a uniform printed graphene pattern where the electrolyte is dropped. Devices with different number of printing layers, from 5 to 20, were reported, having a transmittance ranging from 90 to 71% respectively. Their devices show a single-electrode areal capacitance range from 16 μF/cm^2 at a transmittance of 90 % to a capacitance of 99 μF/cm^2 at transmittance of 71 %. This is the best performance of graphene transparent supercapacitors reported in the literature. This technique is particularly interesting because it allows the facile and scalable fabrication of on-chip energy storage components for emerging electronics and enables new applications where transparency and/or flexibility is required.



Process flow of the fabrication of the transparent micro-supercapacitors. Illustration: Adapted from [1]

[1] S. S. Delekta *et al. Nanoscale* **9**, 6998 (2017)

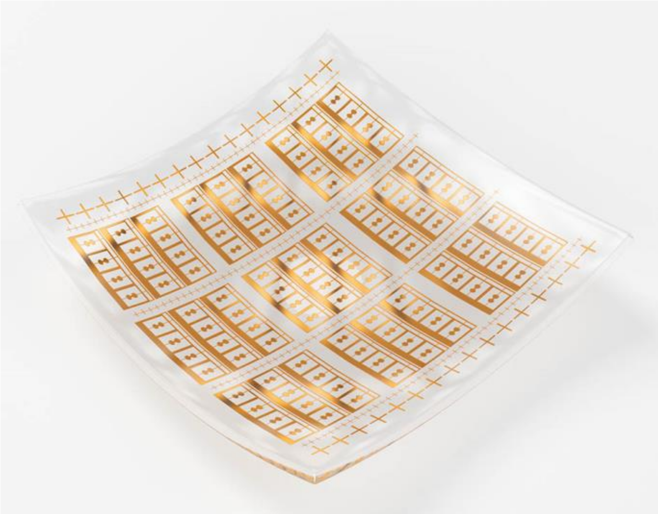
Electronics

Terahertz detectors

There is a growing interest and need for components working at THz frequencies, mainly due to a demand for higher bandwidth in wireless communications and for imaging applications. Many of these emerging applications call for shape-conforming, lightweight and low-cost detectors, which makes graphene a promising material.

Researchers from Jan Stake's team at Chalmers University of Technology have developed the first mechanically flexible graphene-based terahertz detector. The detector is based on CVD graphene field-effect transistors (GFET) on plastic substrates. The detector works in the frequency range 330 to 500 Gigahertz at room temperature. The voltage responsivity was above 2 V/W and the estimated noise equivalent power (NEP) below 3 nW/$Hz^{1/2}$ at 487 GHz.

X. Yang *et al. App. Phys. Lett.* **111**, 021102 (2017)



With the help of the two-dimensional material graphene, the flexible terahertz detector has been developed by researchers at Chalmers.
Illustration: Boid – Product Design Studio, Gothenburg/Chalmers University of Technology.

See the video on Youtube about the new technology >>

In a similar study, the same scientists used graphene on silicon substrates, which resulted in a stiff device. However, the GFET detector performance was considerably higher. The responsivity of the detector was 74 V/W and the NEP was as low as 130 $pW/Hz^{½}$ at 400 GHz. The key factors to reach these high values was the high quality of the graphene and minimization of contamination during the fabrication process.

A. Generalov *et al. IEEE Trans. THz Sci. Technol.* **7**, 614 (2017)

Printed textile electronics

The previous edition of this Research Intelligence Report (no 1, 2017) highlighted that printed transistors consisting entirely of 2D materials now have been fabricated. Another step towards fully printed wearable electronics have now been taken; flexible and washable field-effect transistors (FETs) have been inkjet-printed on fabrics. The devices were based on non-toxic, low boiling point inks of graphene and hexagonal-boron nitride (h-BN) and were printed on polyester textile. The graphene/h-BN heterostructure FETs showed a mobility of 90 $cm^2V^{-1}s^{-1}$, at low voltage (<5 V) in ambient conditions, could withstand up to 4 % strain and were washable for at least 20 cycles.

The inks were used to print entire integrated electronic circuits combining active and passive components. Unlike these flexible circuits, most other wearable electronic devices rely on some rigid components which limits the usability in wearables.

T. Carey *et al. Nat. Commun.* **8**, 1202 (2017)

Composites

Anisotropic composite

An efficient and even dispersion of graphene (and other nanoparticles) in polymer nanocomposites is considered an industry-wide challenge. In some applications it can be advantageous to keep the inherent anisotropy of the two-dimensional graphene. Gaska *et al.* at Chalmers University of Technology used a melt extrusion process to produce LDPE-composites (low-density polyethylene) with a good filler dispersion and strong anisotropy. This created a tortuous path for permeation of gas molecules through the bulk of the composite. A reduction of the permeation of CO_2 by 35 % using 1 % GNP (graphene nanoplatelets, i.e. consisting of more than 10 atomic layers) and 66 % with 7.5 % GNP was shown. The improvement is even higher for larger gas molecules as it is a mechanical and geometrical effect. The permeation of SF_6 was reduced by 62 % and 81 % for composites with 1 and 7.5 % of GNP, respectively. The thermal conductivity of the composite with 7.5 % GNP was increased by a factor four in the plane, whereas the through plane conductivity was slightly reduced.

K. Gaska *et al. Polymers* **9**, 294 (2017)

Non-destructive characterisation

New ideas on how to characterise the dispersion of graphene in the polymer matrix are emerging. Old techniques often rely on investigating cross-sections of the composite with electron microscopy. However, these techniques can only analyse a small part of the sample and also destroy the investigated material.

One new method utilizes that graphene in the matrix can improve the thermal conductivity. The level of improvement is dependent on the loading and on the distribution of graphene. The new method therefore exploits an infrared thermography mapping technique that estimates the dispersion by measuring the thermal diffusivity. This method is non-contact, works at the macroscale and is relatively cheap.

M. Gresil *et al. Scientific Reports* **7**, 5536 (2017)

Flame retardants

Brominated compounds have been widely used as effective flame retardants. However, they have been banned after having been found to be toxic. This has created a need to develop new flame retardants. For many applications these need to have a low density and high mechanical strength. Different combinations of polymer foams with for example inorganic compounds or carbon nanomaterials have been developed. It has however been difficult to produce these with desired properties using a scalable and low-cost technique. Nevertheless, flame retardant polyimide foams incorporated with graphene hybridized with red phosphorous have now been developed using an industrially compatible ball milling process.

The phosphorous quickly oxidises when heated, which promotes formation of char. As graphene is chemically stable at high temperature, the char and the graphene combines to create an oxygen-proof layer on the surface, which stops the underlying material from burning. Even a low concentration of graphene (2.2 wt %) resulted in a higher oxygen limiting index than those of traditional flame-retardant polymer-based materials. Additionally, the material was lightweight and had high compressive strength.

L. Xu *et al. ACS Appl. Mater. Interfaces* **9**, 26392 (2017)

Graphene cement composite

A recent study has investigated the rheological properties of graphene cement paste. Several models were tested and it was found that the Modified Bingham model best fitted the experimental flow curves. It was found that the yield stress increased with the content of graphene nanoplatelets (GNP) in the composite and with the resting time. The GNP cement based composite showed a 30 % increase in load carrying capacity and 73 % increase in overall failure strain.

The addition of graphene into the concrete also enhances the electrical conductivity. Since the resistance increases if any cracks start to form, a self-sensing composite can be made by monitoring the resistance. It was found that the electrical resistivity was reduced by 42 % at maximum compressive load. Graphene cement composites can thereby be used to monitor the structural health of the concrete.

S. K. U. Rehman *et al. Sustainability* **9**, 1229 (2017)

Silk reinforced with graphene

Silk from silkworms have been used for a very long time. Spider silk is also getting an increasing interest owing to its even better mechanical properties. Recent studies have investigated how to increase the mechanical properties even further by incorporating graphene into the silk. The graphene was added into the silk by feeding the silkworms and spiders with aqueous dispersions of graphene and carbon nanotubes. The resulting silk had a fracture strength of 5,4 GPa (whereas pristine spider silk is at the level of 1.5 GPa) and a toughness modulus of 1570 J/g (whereas pristine spider silk is around 150 J/g). It was found that carbon nanotubes were more effective at improving the mechanical properties than the graphene, most likely due to the two orders of magnitude larger characteristic dimension of the nanotubes (0.2-0.3µm of the graphene). The researchers discuss that this process of reinforcing biological materials can be extended to other animals and plants and lead to a new class of artificially modified biological materials.

E. Lepore *et al. 2D Mater.* 4. 031013 (2017)
Qi Wang *et al. Nano Lett.* 16 6695-6700 (2016)

Biotechnology

Neural Interfaces

Many properties of graphene and graphene-based materials make them a potential platform that could address many of the current challenges in neural interface design: flexibility, electrical mobility, large surface area and possible functionalization. A recent review article outlines how these properties can enable enhanced functional capabilities for neural interfaces. For example, graphene-based microtransistor arrays can be used as flexible brain sensors with high spatial resolution. Graphene-based porous material, offering charge injection capacitances similar or superior to other more conventional materials, could also be used in neuro-stimulation devices.

K. Kostarelos *et al. Adv. Mater.* **29**, 1700909 (2017)

Biosensing

Label-free detection of charged molecules can be made using the concept of ion sensitive field effect transistors (ISFET): when a molecule binds to the sensor surface, it modulates the electrical current in the active part of the sensor due to the field effect, allowing it to be detected. Using graphene, a very sensitive material, in this type of sensor, can further increase its sensitivity. Conventionally, graphene-based ISFET sensors are biased at the highest possible transconductance[3], which also yields the highest response. The electronic noise is unfortunately also large at this bias point, limiting the sensitivity of this type of sensor.

In a recent paper, researchers show that this noise can be significantly lowered by operating the sensor using an AC (alternating current) lock-in technique while biasing the sensor close to the neutrality point of graphene. Indeed, their study shows the amplitude of the noise as a function of the bias and confirms that there is a minimum at the neutrality point of graphene. On the one hand, noise decreases and on the other the sensing response is similar, doubling the signal to noise ratio in comparison with the conventional configuration. The potential use of this type of device was demonstrated by using it as a selective and ultrasensitive DNA sensor. The graphene region of the ISFET was functionalised to make it selective to a certain strand of DNA molecule. A clear signal was detected only in the presence of the right type of molecules and for low molecule concentrations (10 pM). The amplitude of the noise, 0.1 nA, was also significantly reduced when compared to the value obtained in a conventional graphene device (0.22 nA) with similar sensing response, confirming the potential of this type of sensors for low-noise applications.

Wangyang Fu *et al. Sci. Adv.* **3**, e1701247 (2017)

Bioscaffolds

When living cells are missing or damaged, an artificial structure, called bioscaffolds, can be implanted to support the regrowth of cells and tissues and can be made of several types of natural or synthetic material. Hydrogels are synthetic polymeric materials routinely used as

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[3] The transconductance is the electrical characteristic relating the current through the output of a device to the voltage across the input of a device. A higher transconductance therefore signifies a stronger coupling between input and output.

scaffolds for the growth of all types of cells. Their porous structure makes them an interesting platform as this allows them to resemble real soft tissue. Unfortunately, the polymers commonly used in hydrogels have low mechanical strength. The addition of nanosized material to the polymer matrix does not only reinforce and improve the mechanical strength. In addition to providing a physical support to cell growth it also potentially adds synergistic benefits and provides novel features to the scaffolds. Previous studies have focused on the use of graphene oxide (and reduced graphene oxide), since these additives are relatively simple to obtain. In a recent article, researchers studied the ability of graphene-based polyacrylamide hydrogels to support the growth of living primary neurons. Changing the concentration of graphene in the hydrogel, they were able to show that the hydrogel's pore size is modulated by the quantity of graphene: the higher the graphene concentration, the smaller the pore size. This correlation makes it possible to tailor swelling and mechanical properties of the hydrogel, which they also showed. The researchers also confirmed that the incorporation of graphene in the hydrogel increases the toughness of the hydrogel by roughly 70 % without any sign of fatigue, even after 100 compression cycles. The growth of neuronal cells was then tested on bare and graphene-based (with a concentration of 0.2 mg/mL) hydrogels and showed that neurons only grew in the scaffolds where graphene was used as an additive. This seems to indicate that the presence of graphene inside the structure of the hydrogel has an intrinsic beneficial role.

C. Martin *et al. Scientific Report* **7**, 10942 (2017)