1.3.12 Scalable high-mobility graphene for photonics and biomedicine

Often mentioned as the "wonder material", graphene, has shown a cornucopia of new physics and potential novel applications. Years after its discovery, although basic science is definitely still not exhausted, there is a great possibility to demonstrate technologically viable high-tech applications in fields such as photonics and biomedicine. For most of these applications scalable high-mobility graphene is necessary. Here, we demonstrate different approaches that yield wafer scale production of graphene with qualities comparable to those of flakes obtained via mechanical exfoliation. We report high-performance photonic devices and possible biomedical applications.

Photonics is an extremely promising realm of applications for graphene, whose lack of bandgap strongly hinders its use in conventional digital logic devices. The same lack of bandgap makes graphene a unique broadband absorption material that further presents electro-absorption and electro-refraction for modulators and switches and photo-thermoelectric effect for detectors. Also, graphene holds the potential to overcome the present limitations of optical interconnects in Datacom and Telecom communications by providing integrated optical components with superior performances, reduced cost, minimal power consumption and footprint. This potential could be however unfulfilled if high-carrier mobilities (above 10 000 cm^2/Vs @ 10^{12} cm^{-2} at room temperature (RT)) are not demonstrated over wafer-scale and on technologically relevant substrates, thus ensuring competitive modulation, detection and switching performances. Graphene exfoliated flakes present an extraordinary mobility thanks to their high crystallinity and only when devices are fabricated in ideal conditions (i.e., flakes are suspended or encapsulated in extremely flat, clean and low-interacting materials) so that carrier transport is not disrupted. In 2014 there was still no viable approach in literature to obtain high mobility graphene over wafer-scale because fundamental issues in the growth, transfer and interface control of graphene needed to be solved. At NEST, we have demonstrated in the last years the synthesis of wafer-scale graphene with carrier mobilities comparable to those of exfoliated flakes and that this mobility can be preserved in devices by finely engineering graphene interface with bulk substrates and overlayers.

In first instance, we perfectioned the synthesis [1-3] and investigated the photonic performance of graphene synthesized via different approaches on silicon carbide (SiC) [4-6]. In 2014, this synthetic approach was the most promising to obtain graphene with high carrier mobilities on a scalable substrate. The observation of THz saturable absorption [4, 6] and THz detection [5] further stimulated our efforts to find alternative ways to synthesize scalable graphene for photonic applications. Indeed, SiC is an expensive substrate and considered a niche material for technological applications.

We hence started to perfect growth of graphene on copper (Cu) foil, a substrate that allowed at the time to obtain polycrystalline graphene that could be transferred to any target substrate. We first demonstrated the synthesis of large single-crystals of graphene (up to 4 mm in size) on Cu foil via chemical vapor deposition (CVD) by carefully controlling the substrate chemistry and growth conditions [7]. On these single-crystals, high performing devices with notable electrical performance could be obtained [8]. We subsequently demonstrated a novel approach which led to the first report of deterministically grown single-crystal graphene arrays with dimensions suitable for the realization of photonic devices (i.e., each crystal being hundreds of micrometers) (see Fig. 1) [9]. Such seeded growth approach allows one to obtain high-mobility single-crystal graphene exactly where is needed (i.e., seed deposition is implemented according to the design and placement of the final devices). We presented a protocol to deterministically transfer the arrays to the target substrate, where photonic components can be realized each on a single crystal. Graphene RT mobilities approach 10 000 cm^2/Vs on conventional SiO_2/Si substrates and are above 20 000 cm^2/Vs on hBN [9].

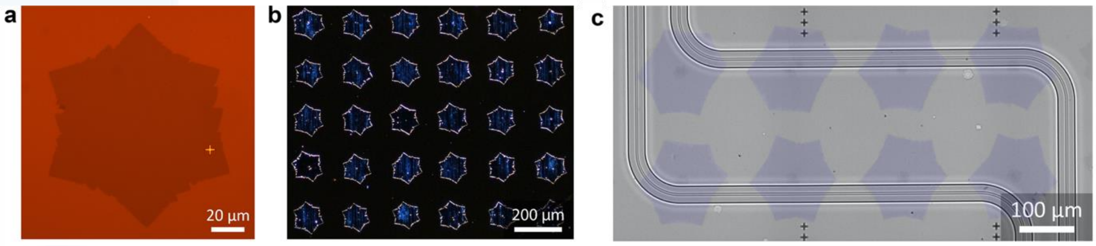

Figure 1. (a) Optical image of a typical single-crystal deterministically grown within an array on Cu foil and transferred on 285 nm SiO_2. (b) Dark-field microscopy image of a graphene array. (c) False color optical image of an array transferred on top of two adjacent waveguides.

By using these graphene matrixes, we have demonstrated high-performance photonics building-blocks such as modulators and detectors [10-12]. In particular, in collaboration with commercial partners such as Nokia and Thales, we have demonstrated ultrafast electro-absorption modulators (working at 50 Gb/s) [10] and photodetectors (with a flat band response up to 67 GHz) [12] integrated on silicon passive waveguides. To preserve graphene mobility during device fabrication we proposed different solutions: adopting a polymeric top dielectric (whose deposition does not damage graphene) [12] or a sacrificial 2D layer prior to dielectric deposition [10]. Several other novel photonic geometries and devices have been demonstrated by adopting graphene synthesized on copper [13-15]. We have also recently demonstrated that the electronic properties of the graphene single-crystals are entirely equivalent to those of exfoliated flakes [16]. We have shown that, in hBN-encapsulated CVD-graphene single-crystals, mobilities exceed 140 000 cm^2/Vs at RT (600 000 cm2/Vs at low temperature) and that signatures of electronic correlation, including the fractional quantum Hall effect are observed under magnetic fields [16].
Although graphene matrixes grown on Cu hold great potential for photonics, the back-end-of-line (BEOL) integration of this material might encounter problems if the amount of Cu contamination is above the allowed limits. To overcome this hurdle, we recently proposed and demonstrated an elegant solution that makes graphene a fab-compatible material while maintaining satisfying electronic performances over wafer-scale. In Ref. [17] we demonstrate for the first time the metal-free growth of monolayer graphene on 4-inch and 6-inch sapphire wafers and identified the sapphire surface reconstruction $(\sqrt{31}\times\sqrt{31})R9°$ as crucial to obtain high-quality epitaxial graphene. To broaden the applicative range of the grown material, we demonstrated that entire wafers of graphene can be transferred to any target substrate with a metal-free polymeric lamination approach. A high degree of uniformity and consistency, which is crucial for any industrial process, was observed in all produced graphene wafers (Fig. 2) and the

measured metal contamination levels was found to fully satisfy BEOL integration requirements.

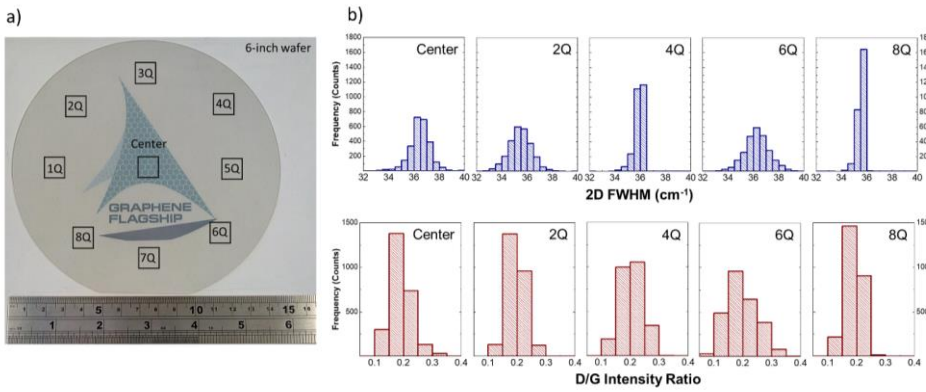

Figure 2. Characterization of graphene grown on 6-inch sapphire wafer. (a) Optical image of the grown wafer, with squares indicating the approximate locations where Raman measurements were performed. (b) Raman analysis of graphene grown on a 6-inch sapphire wafer, measured at 5 different places.

Graphene could also become a central material in biomedicine, due to its exceptional electrical, optical and tribological properties. On this regard, its biocompatibility, transparency and high electrical conductivity make it an interesting candidate for the development of biosensors. On this topic, we have patented a platform for the isolation from biological fluids and characterization by optical and biological assays of exosomes, which are early-stage cancer markers [17]. Also, we have investigated graphene potential for the development of novel neural conduit for regenerative medicine. In Ref. [18], we reported increased elongation and differentiation of peripheral neuronal cells grown on graphene. However, to date, the molecular mechanism driving axon elongation had remained elusive. Hence, we studied the axonal transport of nerve growth factor (NGF), the neurotrophin supporting development of peripheral neurons, as a key player in the time course of axonal elongation of dorsal root ganglion neurons on graphene [19]. We found that graphene drastically reduces the number of retrogradely transported NGF vesicles in favor of a stalled population in the first 2 days of culture, in which the boost of axon elongation was observed. Targeted spectroscopic, ultrastructural and electrophysiological studies indicate that both electrophysiological and structural effects account for graphene action on neuron development [19].

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