Atomically Precise Graphene Nanoribbons for Device Applications

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Graphene nanoribbons (GNRs) are narrow strips of graphene which, due to lateral confinement, have an appreciable bandgap, thus making them suitable for room temperature switching device applications. Investigation of GNRs has initially focused on top-down methods such as lithography of graphene, though bottom-up synthesis by polymerization and surface assisted cyclodehydrogenation (Figure 1a) has advantages over such methods because of the atomically precise edge structure and narrower widths which are achievable (Figure 1b, c) [1]. However, fabrication of the highest quality bottom-up GNRs is done under ultra-high vacuum conditions (10^{-11} mbar) which is incompatible with an industry level production process. Additionally, transfer of GNRs from the metallic growth substrate (herein Au/mica) to technologically relevant substrates is required to exploit the GNR properties for a given device application. This contribution addresses some of the issues regarding scalability and industrial viability of GNRs, as well as transfer to arbitrary substrates and prototype device work.
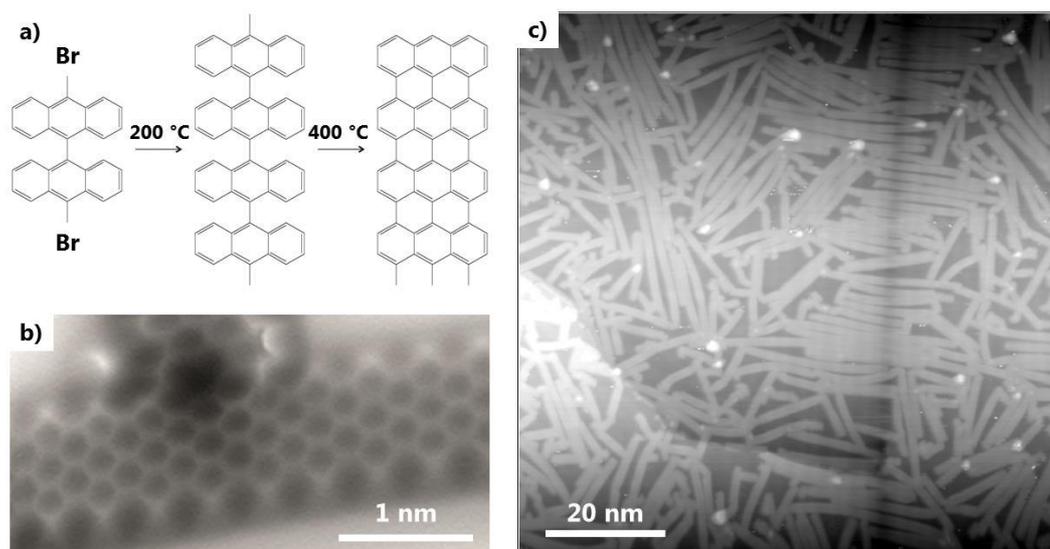

Figure 1: Bottom-up synthesis of a 7-AGNR on Au(111) (a), non-contact atomic force microscopy (b), and scanning tunneling microscopy (c) of synthesized GNRs [1].

The nanotech@surfaces laboratory at EMPA has constructed a dedicated GNR fabrication system which runs on software controlled pre-defined growth recipes, and is capable of depositing precursor molecules over a relatively large area (20x20 mm^2). This allows a significant increase in the GNR production rate, which is necessary for ambient characterization and device work. Production is currently focused on 7-AGNRs (a 7 carbon wide GNR with armchair edges) as a model system for development. GNR quality as determined by Raman spectroscopy is homogeneous across the 20x20 mm^2 deposition area, as well as reproducible between production runs.

As a potential industrial production process, the use of less stringent vacuum conditions (10^{-6} vs 10^{-11} mbar) would be more ideal. Base vacuum for GNR synthesis was explored across this

range, and a critical partial pressure of water and oxygen at which point dendritic (instead of ribbon) growth occurs was determined. In addition to lower vacuum conditions for synthesis, GNRs should be stable under ambient conditions, at least until device fabrication and encapsulation is completed. 7-AGNRs were found to be stable for several months under such conditions, with minor alterations to the Raman characteristics of the ribbons. The most notable changes were an increase in the full-width-at-half-max of all peaks and a blue-shift of the G-peak. The time frame for this peak shift is highly dependent on the total coverage of the GNRs, indicating that it is related to adsorption or intercalation of hydrocarbons and/or water from the atmosphere. In fact, heating of the GNRs to remove these contaminants leads to recovery of the initial G-peak position. The most important result of the long-term stability study was the persistence of a strong radial-breathing-like-mode even after several months; this peak is characteristic of the GNR width, and indicates that they retain their structural integrity over time.

Production is just the starting point of a GNR technology, and GNRs must be transferred to semiconducting or insulating substrates for device applications. Membrane-assisted transfer (i.e. PMMA) has limited potential due to polymer contamination and tearing of the GNR film. Non-membrane methods can reduce contamination and are also possible over large areas. By placing the GNR/Au/mica sample in HCl, detachment occurs at the Au/mica interface leaving a floating GNR/Au film [2]. This film can be transferred to an arbitrary substrate (i.e. SiO_2), and the Au growth/support film can be etched away (Figure 2a, b). There is no residual contamination or significant degradation of GNR quality from the transfer process, so such a method is viable for fabrication of prototype GNR-field-effect transistors (FET) (Figure 2c) using e-beam lithography followed by metal evaporation and lift-off.

Initial progress on 7-AGNR-FETs is limited by a very large contact resistance due to a Schottky barrier from the high bandgap of the 7-AGNR [3]. Several materials-related and process-related strategies are being investigated to overcome this limitation and demonstrate the potential of GNR-FETs [4].
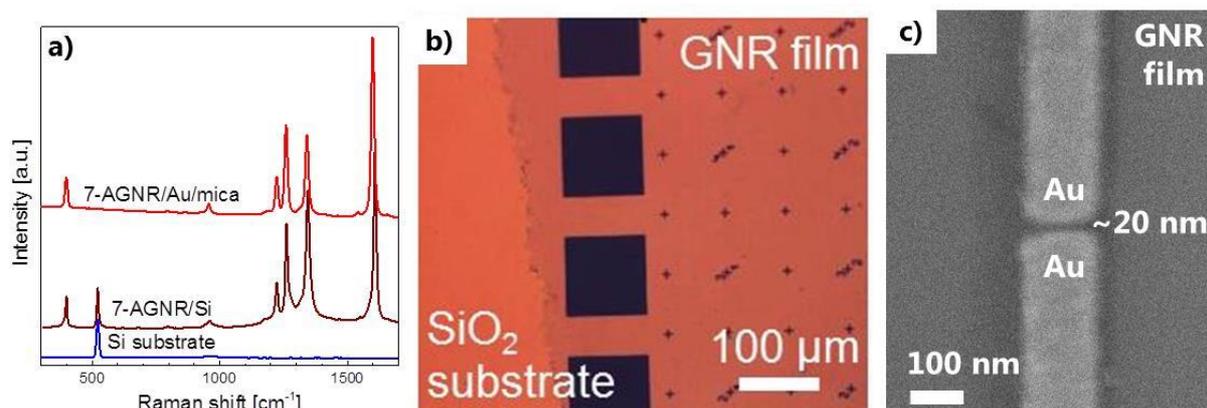

Figure 2: Raman of 7-AGNRs before and after transfer to SiO_2/Si (a), micrograph of 7-AGNR film transferred to SiO_2/Si (b), electrode geometry of a back-gated GNR-FET device (c).

References
[1]   J. Cai et al., Nature 466 (2010) 470.
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[3]   P.B. Bennett et al., Appl. Phys. Lett. 103 (2013) 253114.
[4]   This research was supported by BASF, the SNF, and the ONR BRC program.