

Rapid and Scalable Fabrication of Patterned Graphene Structures Using Imprint Lithography and Polymeric Precursors

Uzodinma Okoroanyanwu, Ayush Bhardwaj, Vincent Einck, James J. Watkins

Department of Polymer Science and Engineering, University of Massachusetts Amherst,
Amherst, Massachusetts 01003, United States

ABSTRACT

We report a fast, efficient, and scalable direct imprint lithographic process for fabricating patterned graphene structures from a variety of polymeric precursors. The process involves soft lithographic imprint patterning of appropriate polymeric films on suitable substrates including silicon wafers and stainless-steel foils, using fluorinated solvent permeable patterned poly(dimethyl siloxane) stamps, while simultaneously curing the films at appropriate temperatures. Next, the cured films are subjected to photothermal pyrolysis in air using high intensity xenon flash lamp to yield patterned graphene structures, without the use of a catalyst. Fluorination of the stamp ensures a smooth release of the stamp at the end of the imprint process, without damaging the imprinted features. Thermal curing at 220 °C yields structures that are structurally stable to photothermal pyrolysis in air at temperatures of up to 1500 °C. Structures of various geometries including lines, holes, trenches, etc., and length scales ranging from nanometers to millimeters, are readily realized with this technique in a few minutes. Suitable precursor polymers have absorption spectra with peak maxima that overlaps the emission spectrum of xenon flash lamp, and these include polybenzoxazine, phenol-formaldehyde resin, and others. The microstructure and physical properties of the graphene features can be controlled via pulse power modulation. The choice of photonic processing using xenon flash lamp instead of laser offers several advantages in terms of reduced cost and complexity, improved efficiency in converting electrical energy to light, and scalability to large area processing without rastering. The direct fabrication of patterned high quality graphene structures is amenable to roll-to-roll processing and offers significant opportunities for scalable fabrication of graphene-based electronic devices with applications in printed, wearable, organic, flexible, and flexible/hybrid electronics; electrochemical energy storage, photovoltaics, electroluminescence, gas sensing, composites, thermal management, electromagnetic interference and electromagnetic pulse shielding, and other fields.

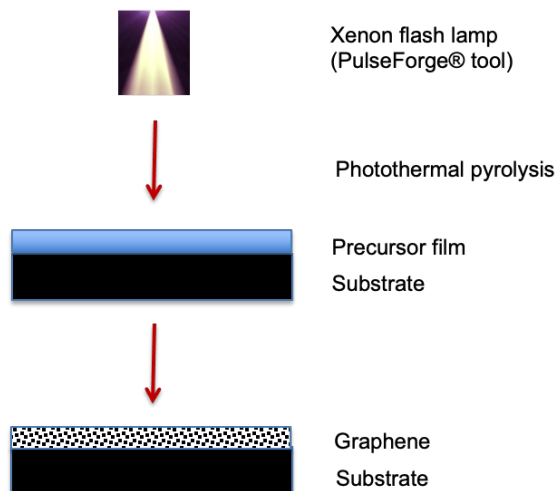


Figure 1. Schematic of the photothermal pyrolysis process

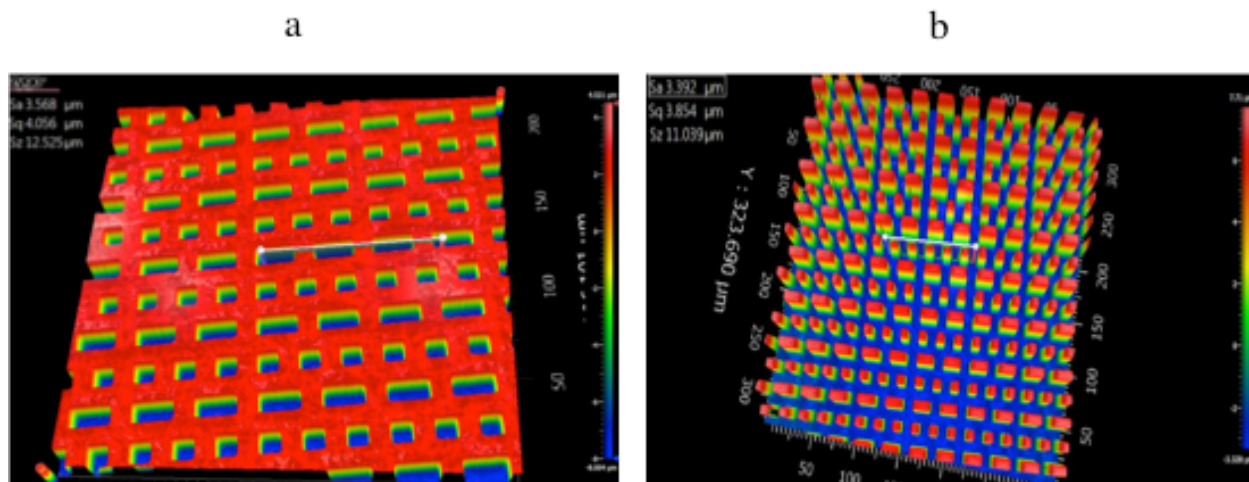


Figure 2. Three-dimensional optical profilometric images of (a) silicon master used in patterning poly(dimethyl siloxane) stamp, (b) poly(dimethyl siloxane) stamp used in patterning polymeric precursors of graphene structures.

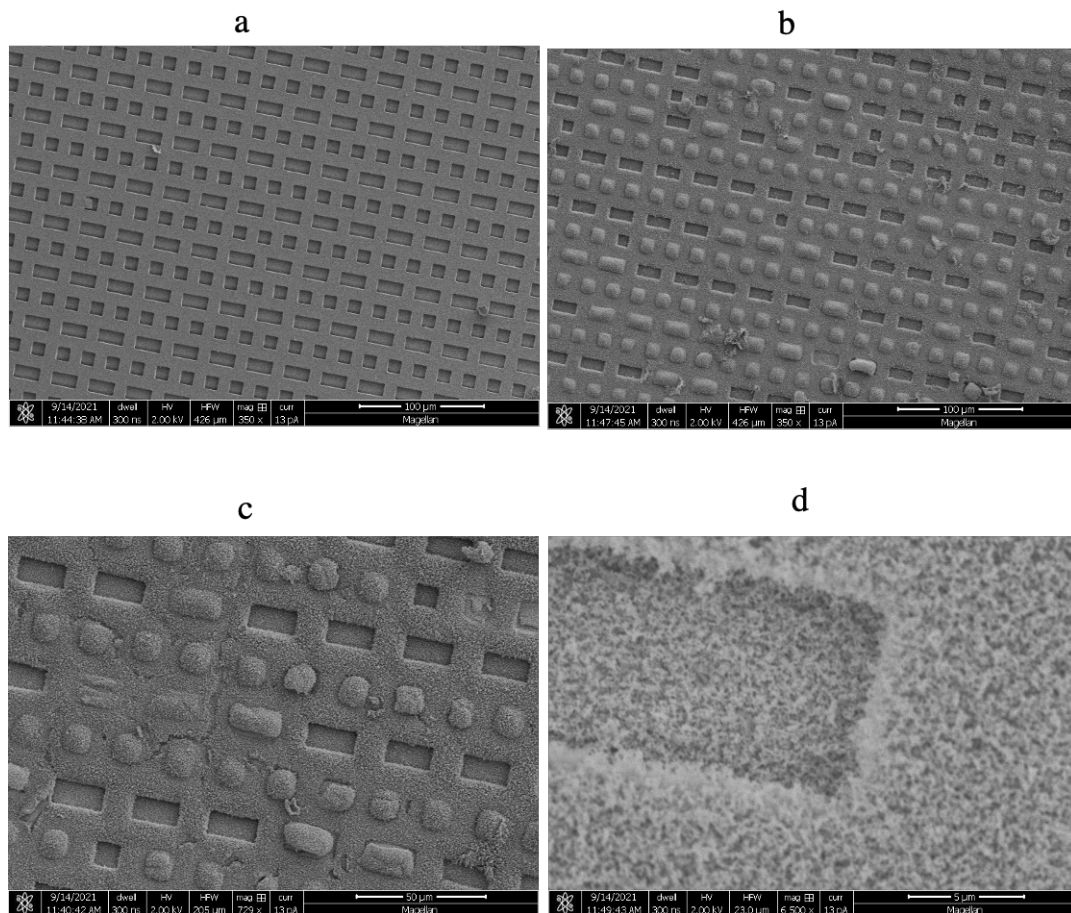


Figure 3. SEM images of imprinted and thermally cured structures, and graphene features derived from them upon photothermal pyrolysis in air. (a) thermally cured imprinted features, (b) graphene features derived via photothermal pyrolysis of features shown in Figure a, (c and d) magnified images of features in Figure b. Graphene flakes and platelets, grey in color, decorate the patterned features. Features include lines, square holes, and trenches. Some of the imprinted features are covered by graphene flakes and platelets, if the size of the features is smaller than that of the graphene flakes and platelets.

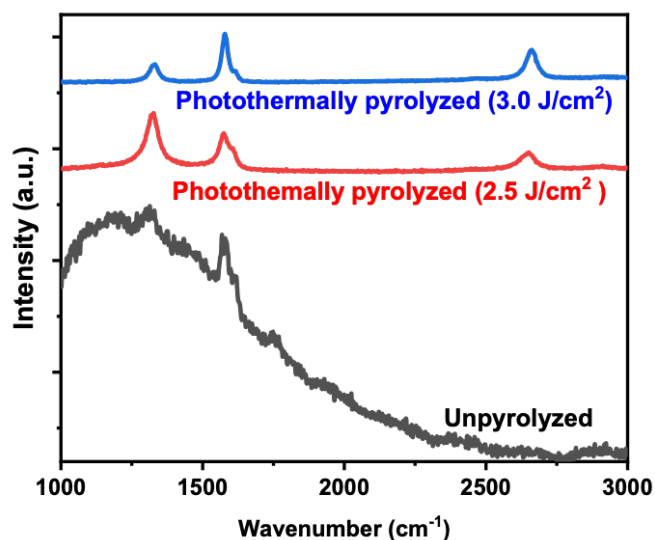


Figure 4. Raman spectra of imprinted and thermally cured structures, and graphene features derived from them upon photothermal pyrolysis in air, using 70 xenon flash lamp pulses with 500 μs pulse length, 520 V, and corresponding to energy density of 2.5 J/cm^2 per pulse; 70 xenon flash lamp pulses with 500 μs pulse length, 560 V, and corresponding to energy density of 3.0 J/cm^2 per pulse. The spectra obtained on the photothermally-pyrolyzed samples show characteristic graphitic bands near 1582 cm^{-1} (Graphitic, G-band) and 1350 cm^{-1} (Disorder, D-band). The ratio of the intensity of the D-band relative to the G-band is a good measure of the quality of the graphitic carbons in the sample. If this ratio is less than unity as in the sample pyrolyzed with 3.0 J/cm^2 , the sample has high degree of structural order and has a high quality graphitic phase. If the ratio is greater than unity as in the sample pyrolyzed with 2.5 J/cm^2 , the sample has a high degree of structural disorder. The peak near 2700 cm^{-1} (2D-band) is an overtone of the D-band, and it is also characteristic of graphite, specifically, graphitic ordering of free carbon along the free axis. That this peak can be fitted with a single Lorentzian peak is indicative of the presence of high-quality graphene in the sample. The size of this peak relative to the G-peak is also a good measure of the number of graphene layers present in the sample. That the ratio of the 2D-peak to the G-peak is less than unity is indicative of the presence of few layer graphene in the sample. The quality of the obtained graphene improves with the pulse power density used in the pyrolysis of the precursor film.