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# Mechanical characterisation of nanocrystalline graphite using micromechanical structures

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ABSTRACT

Conductive nanocrystalline graphite has been deposited using plasma-enhanced chemical vapour deposition at 750 °C, directly onto silicon substrates without any catalyst and fabricated into micromechanical membrane and beam structures. Using the buckling profile of the membrane and beam structures, we measure a built-in strain of −0.0142 and through wafer-bow measurement, a compressive stress of 436 MPa. From this we have calculated the Young's modulus of nanographite as 23.0 ± 2.7 GPa. This represents a scalable method for fabricating nanographite MEMS and NEMS devices via a microfabrication-compatible process and provides useful mechanical properties to enable design of future devices.



## 1. Introduction

Graphene, thin-film graphite and graphene derivatives such as graphene-oxide (GO) are promising carbon based materials for micro and nano-electromechanical systems (MEMS/NEMS), and also as passive freestanding structures such as gas filtration membranes. The main properties of interest include good mechanical stiffness and strength [1] and electrical conductivity [2].

For example, graphene sheets and GO have been demonstrated as NEMS resonators [1,3,4] for high frequency sensors and signal processing applications; where the high stiffness and ultimate thinness are attractive for high sensitivity devices. GO is also of high interest for molecular filtration membranes [5,6] where molecules selectively pass through the defects in the crystal structure.

Currently the most widely used synthesis methods for large-scale graphene require a catalyst, for example copper or single-crystal germanium, and a subsequent transfer process onto the device substrate [7–9]. This is not cost-effective and can introduce defects such as wrinkling and polymer contamination. GO is typically synthesised through exfoliation of graphite-oxide [10], which then requires a transfer through manual adhesion, and typically when produced on a large-scale has thickness variations. This processing route represents a significant departure from standard microfabrication technologies.

Related materials such as amorphous tetrahedral-carbon and diamond-like carbon are readily deposited on a wafer-scale by methods including pulsed laser deposition and filtered cathodic vacuum arc [11–14]. Such films have had application particularly for devices where low friction is of interest [11,12] however typically have relatively poor electrical conductivity and extremely high intrinsic stress (>1 GPa) which leads to poor substrate adhesion, this has limited their use somewhat within released and freestanding MEMS applications.

As an alternative carbon-based material, plasma-enhanced CVD (PECVD) using methane as a carbon precursor provides a scalable, microfabrication-compatible method to deposit nanocrystalline graphene (nanographene) and nanocrystalline graphite (nanographite) thin films directly onto insulating substrates such as silicon and silicon dioxide ($SiO_2$) [15–20] thereby removing the need for transferal of the film between substrates. Nanographite films typically have crystallites on the order of 10 nm, and a higher electrical resistivity compared with pristine graphene. Nanographite has been shown to have promising performance for transparent electrode applications [15,16], as a strain sensor due to its high piezoresistive coefficient [17], in photovoltaics [18], in electronics [19], and as a potential material for MEMS/NEMS applications [20].

In this work, the fabrication of micromechanical structures and mechanical characterisation of PECVD nanographite is presented. The stress is extracted using wafer bow measurements and the Young's

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modulus of nanographite is then calculated using the buckling effect of both micromechanical membranes and doubly-clamped beams. These fundamental mechanical properties are essential for the future design of MEMS and NEMS using nanographite, and demonstrate a simple route for fabricating released structures. This represents a useful addition alongside the development of graphene, GO and other carbon materials, whereby some of the material properties are exchanged for the much greater ease of fabrication and integration afforded by catalyst-free PECVD.

## 2. Materials and methods

### 2.1. Film characterisation

Raman spectroscopy (Renishaw inVia) was used to characterise the structural properties of the nanographite film, using 532 nm wavelength excitation laser.

In order to image the material topology, a scanning electron micrograph of the film was taken using JEOL JSM FESEM 6700F at 80,000 times magnification. An atomic force microscope (Bruker Multimode AFM) in contact mode was used over a $1 \times 1$ μm scanning area to measure the film roughness.

The buckling amplitude of square nanographite membranes and beams were analysed using white-light interferometry (Polytec MSA-400). The thickness of each membrane was measured using ellipsometry (J. A. Woolham M2000), and side length was measured using optical microscopy. The stress of the nanographite film was determined using the wafer bow technique, a commercial measurement tool (KLA FLX) was used for bow measurement.

The electrical conductivity of the film was measured using micromachined 'transmission-line model' structures [21], with nickel/titanium electrodes of increasing separation (20 to 100 μm separation) deposited onto an electrically isolated mesa of the nanographite film. I—V characteristics were obtained using a 'Cascade Microtech' probe station and 'Agilent B1500A Semiconductor' network analyser. A voltage sweep between - 10 and 10 V was applied.

### 2.2. Micromechanical device fabrication

A commercial PECVD tool (Oxford Instruments Nanofab1000 Agile) was used to deposit nanographite onto 6-in. silicon wafers. The deposition conditions are summarised in Table 1. The hydrogen acts as a diluent, controlling deposition rate and promoting graphitic carbon growth by etching amorphous carbon [16]. The relatively high deposition temperature of 750 °C was used, since this was the minimum temperature to obtain graphitic carbon growth, below which amorphous carbon or no deposition occurs. Similar PECVD films have growth temperatures ranging from 525 to 900 °C [16,19]. A deposition rate of approximately 2 nm per minute was measured, and the average final thickness of the film was measured across the wafer using white-light ellipsometry.

Fig. 1 shows the main fabrication steps of separate membrane and doubly-clamped beam microstructures. Silicon wafers were first RCA cleaned and then a 400 nm thin film of $SiO_2$ was deposited by PECVD using an Oxford Instruments system 100. For the membranes, 280 nm of nanographite was deposited onto the $SiO_2$ layer (Fig. 1-A). 1.5 μm $SiO_2$ was then deposited using PECVD onto both back and frontside, and squares were patterned onto the backside $SiO_2$ and etched using $Ar/CHF_3$ reactive ion etching (RIE) (Fig. 1-B). The silicon handle was then etched using tetramethylammonium hydroxide (TMAH) leaving 30 μm of silicon. Complete silicon etching was achieved using $Ar/SF_6$ inductively-coupled plasma (ICP) etch until the buried SiO2 film [22]. The buried and front-side $SiO_2$ layers were then etched using RIE, fully releasing the nanographite membrane with side lengths between 190 and 275 μm (Fig. 1-C). An optical microscope image of a membrane is shown in Fig. 2-A.

For the beams, a 200 nm thick $SiO_2$ film was deposited using PECVD and patterned using photolithography and RIE. This creates a sacrificial spacer defining the released beam length (Fig. 1-D). Subsequently, 400 nm of nanographite was deposited over the spacer, and patterned into a beam with large anchors (Fig. 1-E). The nanographite is etched using $O_2$-based RIE. HF vapour, with the sample heated at 40 °C, is then used to isotropically etch the $SiO_2$ spacer and release the beam (Fig. 1-F). Beam lengths between 65 and 140 μm have been fabricated. A scanning electron micrograph of a buckled beam shown is in Fig. 2-B.

**Table 1**
Summary of deposition conditions.

| | |
|---|---|
| Temperature (°C) | 750 |
| Chamber pressure (mTorr) | 1500 |
| $H_2$ flow (sccm) | 75 |
| $CH_4$ flow (sccm) | 60 |
| RF Power (W) | 100 |

## 3. Theory/calculation

### 3.1. Membrane buckling

The buckling behaviour of square micromechanical membranes has been utilised as a method to characterise the Young's modulus of, for example, $Si_3N_4$ membranes [23,24]. Here, the buckling characterisation of membranes will be applied to nanographite membranes, such as shown in Fig. 2-A, for the calculation of the material Young's modulus.

The geometry of compressively stressed square membranes has been shown to lie within 3 regimes, defined by their buckling shape, depending on the level of in-plane strain. For regime 1, $\sigma < \sigma_{crit1}$ and the membrane is flat. In regime 2, when $\sigma_{crit1} < \sigma < \sigma_{crit2}$, the membrane is buckled with rotational and four-fold symmetry. In regime 3, $\sigma > \sigma_{crit2}$ and the membrane is buckled with rotational symmetry only. Mathematical analysis using energy-minimisation techniques of the buckling behaviour of square membranes has been undertaken previously by Ziebart et al. [23]. This analysis establishes a relation between the maximum out-of-plane amplitude of a buckled square membrane, and the in-plane strain of the material. The analysis uses dimensionless displacements where the pre-strain $\bar{\varepsilon}_0$ is given in Eq. (1), in terms of the strain $\varepsilon$, side length $a$, and thickness $h$:

$$\bar{\varepsilon}_0 = \frac{\varepsilon \cdot a^2}{h^2} \tag{1}$$

The dimensionless deflection $\bar{w}$ is defined in terms of the real maximum deflection $w$

$$\bar{w} = \frac{w}{h} \tag{2}$$

and a fitted displacement function $\bar{w}_{0fit}$ extracted from energy minimisation is given by

$$\bar{w}_{0fit} = \sqrt{\Delta\bar{\varepsilon}_0 (c_1 + c_2 \tanh\{c_3 \Delta\bar{\varepsilon}_0\} + \frac{\left\{c_4 \Delta\bar{\varepsilon}_0 + c_5 {\Delta\bar{\varepsilon}_0}^2\right\}}{1 - c_6 {\Delta\bar{\varepsilon}_0}^3}} \tag{3}$$

where the fitting parameters $c_1 - c_6$ are calculated as in Eq. (4), where $\nu$ is the Poisson's ratio.

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \\ c_6 \end{pmatrix} = \begin{pmatrix} -0.4972 & -0.2314 & -0.2128 \\ 0.0698 & 0.1625 & 0.200 \\ -7.19 \times 10^{-3} & -0.0466 & 0.0367 \\ -1.19 \times 10^{-3} & 0 & 5.51 \times 10^{-3} \\ -3.34 \times 10^{-6} & -7.43 \times 10^{-5} & 1.28 \times 10^{-4} \\ 3.16 \times 10^{-6} & 4.80 \times 10^{-6} & -1.52 \times 10^{-5} \end{pmatrix} \bullet \begin{pmatrix} 1 \\ \nu \\ \nu^2 \end{pmatrix} \tag{4}$$