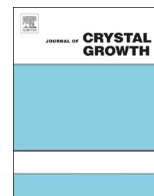




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Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgr

Growth and characterization of 7,7,8,8-tetracyano-quinodimethane crystals on chemical vapor deposition graphene



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ARTICLE INFO

Article history:

Received 15 June 2016

Accepted 19 July 2016

Available online 30 July 2016

Keywords:

A1. Diffusion

A1. Nanostructures

A3. Physical vapor deposition processes

B1. Organic compounds

ABSTRACT

Chemical functionalization of graphene could pave the way for favorably modifying its already remarkable properties. Organic molecules have been utilized to this end as a way to alter graphene's structural, chemical, electrical, optical and even magnetic properties. One such promising organic molecule is 7,7,8,8-tetracyano-quinodimethane (TCNQ), a strong electron acceptor which has been shown to be an effective *p*-dopant of graphene. This study explores the thermal evaporation of TCNQ onto graphene transferred onto SiO₂/Si substrates. Using two different home-made thermal evaporators, a wide range of TCNQ growth regimes are explored, from thin films to bulk crystals. The resulting graphene/TCNQ structure is characterized via optical microscopy, Raman spectroscopy and atomic force microscopy (AFM). Films are found to be comprised of TCNQ and the oxidized product of TCNQ, α,α -dicyano-*p*-toluoyl cyanide (DCTC), which confirms the electron charge transfer from graphene to the TCNQ films. AFM measurements of these films show that after forming a rather smooth layer covering the graphene surface, small clusters start to form. For higher TCNQ coverage, the clusters agglomerate, becoming quite large in size and forming ripples or wrinkles across the surface.

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1. Introduction

In the past decade extensive work has been carried out towards the goal of chemically functionalizing graphene to enhance and complement its remarkable properties [1]. Organic molecules have been used to chemically functionalize through both covalent [2] and non-covalent means [3]. TCNQ is an organic molecule that has been successfully used to non-covalently functionalize graphene. A strong electron acceptor, TCNQ has been utilized to produce highly *p*-doped graphene, resulting in the opening of an electrical bandgap in bilayer graphene [4], and for use as a conductive anode in graphene organic solar cells [5]. Recent studies carried out in ultra-high vacuum have found that TCNQ deposited onto graphene grown epitaxially on ruthenium is able to form extended spin-split electronic bands resulting in long range magnetic order [3]. X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM) measurements confirmed that charge transfer from the ruthenium substrate to the TCNQ, modulated by the

graphene layer in between, caused the molecules to develop a magnetic moment [6,7].

TCNQ and its salts have been studied extensively by Raman spectroscopy, confirming their strong electron accepting capabilities for both films and crystals synthesized by evaporation or from solution [8–13]. Depending on the growth conditions and substrate, the oxidation product of TCNQ²⁻, α,α -dicyano-*p*-toluoyl cyanide (DCTC) is often detected. For TCNQ films evaporated onto Ag, DCTC was detected for thin films, suggesting that the layers close to the Ag substrate were ionized and oxidized. As the TCNQ film thickness increased, DCTC was no longer detected, suggesting that the upper layers of the film were comprised of neutral TCNQ [14]. Similar behavior has been observed via XPS measurements for F₄-TCNQ molecules deposited on epitaxial graphene on SiC. Electron transfer from the graphene to the first few layers of adsorbed F₄-TCNQ was found to *p*-dope the graphene [15]. For CVD grown graphene transferred to an insulating substrate, DCTC was also detected for low coverage, whereas only TCNQ was detected for higher coverages, suggesting a similar mechanism of electron charge transfer from the graphene substrate to the first few TCNQ layers adjacent to it [16].

This study seeks to understand the growth process and morphology of TCNQ evaporated onto Chemical Vapor Deposition (CVD) grown graphene transferred onto SiO₂/Si substrate, which is

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commonly used for device fabrication. Understanding the growth mechanism of TCNQ on graphene is necessary for the further development of devices based on graphene/TCNQ structures, with the hope of exploiting the unique properties of each material. TCNQ films have been shown to be effective graphene dopants as well as exhibiting magnetic properties [3], whereas TCNQ crystals have been shown to have unique electrical [17] and optoelectronic [18] properties when interfaced with adequate complementary organic crystals. Different growth regimes of TCNQ on graphene were explored by varying the sublimation temperature, substrate temperature and vapor concentration of the TCNQ. This resulted in various TCNQ/graphene structures, ranging from thin films to pure TCNQ crystals. Electron charge transfer from the graphene to the TCNQ and subsequent oxidation to DCTC, as previously seen by Qi et al. [16], was confirmed for thin films via Raman spectroscopy. Atomic force microscopy measurements (AFM) showed that at low coverage, the TCNQ films seem to have almost no effect on the graphene surface, whereas for increasing coverage, clusters form, growing in size to the point that they strain the graphene and form filament-like wrinkles.

2. Methods

Graphene was grown on 25 μm thick polycrystalline copper foil via chemical vapor deposition in a CVD furnace. The foil was heated to 1000 $^{\circ}\text{C}$ while flowing 100 standard cubic centimeters (sccm) hydrogen. The temperature was allowed to stabilize for 10 min, before increasing the hydrogen flow to 500 sccm and introducing 1 sccm methane for 25 min in order to induce graphene growth. The furnace was then rapidly cooled to room temperature while flowing 100 sccm hydrogen. The entire process was carried out at 10 mbar. Graphene was then transferred to a highly n-doped silicon substrate terminated with a 300 nm SiO_2 layer. To achieve the transfer, a PMMA layer was spun on the copper foil (about 180 nm thickness), before etching the copper foil in an ammonium persulfate etchant (0.1 g/mL in deionized water). After rinsing the PMMA/graphene stack several times in deionized water, the stack was scooped out with the target Si/ SiO_2 wafer. The graphene was allowed to dry over night before removing the PMMA layer by rinsing in acetone. Thermal annealing was then carried out at 300 $^{\circ}\text{C}$ in Ar/ H_2 96/4% in order to remove remaining PMMA residues. Raman spectroscopy measurements were carried out using a 488 nm laser, with a spot size of about 1 μm using an x80 objective and collected in a cooled silicon CCD detector (Andor Newton), with a 0.5 m spectrometer length and a 300 l/mm grating.

TCNQ evaporation was carried out in a quartz tube placed inside a vacuum desiccator, at a pressure of 600 mbar. For each growth one of two quartz tubes were used, a small one (3.5 cm long, 1.8 cm diameter) or a large one (8 cm long, 2.3 cm diameter), shown in Fig. 1. The lower region of both quartz tubes were heated resistively, by coiling tungsten wire around the exterior of the tubes. 100 mg TCNQ powder (Sigma Aldrich 157,635) was placed inside the bottom of the tube. In order to achieve more homogeneous heating, aluminum foil was also wrapped around the bottom 2 cm of the tubes. An *in situ* thermocouple was used to calibrate the relation between the power dissipated in the resistive coil (usually between 2 and 10 W) and the temperature at the bottom of the tube, and subsequent evaporations were carried out without the thermocouple. The quartz tubes were sealed at their mouth openings with a glass slide, with the graphene/ SiO_2 samples mounted on the glass slide facing the TCNQ powder inside the tube. In the case of the large evaporator, apart from at the tube mouth, samples were also mounted inside the quartz tube 2 cm away from the tube bottom, facing the TCNQ powder, as shown in Fig. 1.

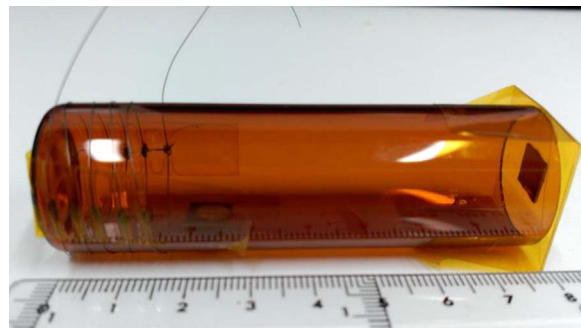


Fig. 1. Picture of large tube TCNQ evaporator with aluminum foil removed from exterior. Samples are placed at the tube mouth and inside the tube, 2 cm away from tube bottom. In the small tube evaporator, the sample is placed only on the mouth of the tube.

3. Results and discussion

Fig. 2 shows white light reflection optical images of TCNQ evaporated onto graphene/ SiO_2 for different sublimation temperatures and growth times in the small tube evaporator. As seen in Fig. 2(a), a growth temperature of 130 $^{\circ}\text{C}$ for 75 min results in the formation of pellet-like crystals on the surface of the graphene, with lateral dimensions on the order of 5 μm . These crystals are separated by a typical distance of a few dozen microns, indicating the high mobility of the individual TCNQ molecules on graphene. Increasing the growth temperature to 160 $^{\circ}\text{C}$ and maintaining the same growth time clearly changes the growth regime, as shown in Fig. 2(b). The graphene substrate is no longer visible and seems to have been covered by a thick film. The morphology of the crystals on the surface has also changed, from pellets to needles with a typical length on the order of 10 μm . The needles are packed more closely together on the surface than the pellets, with many needles touching each other. It seems that the rise in the sublimation temperature substantially modifies the density of TCNQ molecules on the surface. Now the molecules are no longer able to reach the initial condensation points, on the contrary the TCNQ molecules self-assemble, probably via H-bonds [3], forming a full layer that reduces the effective diffusion length of the incoming molecules and as consequence increases the density of 3D islands. From this temperature the growth mode remains unchanged and further increasing the growth temperature to 180 $^{\circ}\text{C}$ completely saturates the graphene surface with TCNQ needles, as shown in Fig. 2(c), despite a reduction in the evaporation time from 75 to 45 min. Evaporating at the highest temperature obtainable in the small tube evaporator, 200 $^{\circ}\text{C}$, for 45 min, maintains the high crystal density on the surface but results in a change in the structure of the crystals, as seen in Fig. 2(d). Apart from needles, many plaque-shaped crystals are seen on the surface, with a typical size of 5–10 μm .

The large tube evaporator (diameter 2.3 cm and length 8 cm) can accommodate two samples simultaneously, one at the extreme of the tube, where the sample remains close to room temperature, and another one inside the tube close to the resistive heating coils, where the sample is heated along with the TCNQ powder. This configuration allows for the comparison of the TCNQ film growth at different substrate temperatures for the same evaporation run. Fig. 3 shows optical images of TCNQ evaporated onto graphene/ SiO_2 for different growth conditions in the large tube evaporator. Fig. 3(a) and (b) show the images corresponding to the substrate placed at the mouth of the tube, where it remains close to room temperature. Evaporating at 120 $^{\circ}\text{C}$ for 60 min results in the formation of TCNQ crystal pellets, as seen in Fig. 3(a). Fig. 3(b) shows that increasing the growth temperature to 170 $^{\circ}\text{C}$ favors the formation of short needles on the graphene surface,

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