

Synthesis and characterization of graphene layers prepared by low-pressure chemical vapor deposition using triphenylphosphine as precursor



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HIGHLIGHTS

- We grow graphene using the solid precursor triphenylphosphine.
- Raman analysis confirms the presence of monolayer graphene.
- SEM images show the presence of small dark areas dispersed on the graphene surface.
- Raman I_D/I_G ratio increases in the dark region of the graphene surface.

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ABSTRACT

The synthesis of a single-layer graphene using a low-pressure Chemical Vapor Deposition (CVD) system with triphenylphosphine as precursor is reported. The amount of triphenylphosphine used as precursor was in the range of 10–40 mg. Raman spectroscopy was employed to analyze samples prepared with 10 mg of the precursor, and these spectra were found typical of graphene. The Raman measurements indicate that the progressive degradation of graphene occurs as the amount of triphenylphosphine increases. X-ray photoelectron spectroscopy measurements were performed to investigate the different chemical environments involving carbon and phosphorous atoms. Scanning electron microscopy and transmission electron microscopy were also employed and the results reveal the formation of dispersed nanostructures on top of the graphene layer. In addition, the number of these nanostructures is directly related to the amount of precursor used for sample growth.

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1. Introduction

In the last decade, graphene has attracted considerable attention due to its potential in a wide range of areas. However, certain applications are limited due to the absence of a band gap in the intrinsic material [1,2]. Several approaches have been studied to improve and control graphene properties, such as geometrical tailoring of the sheets [3] and chemical doping [4]. One of the most feasible methods for controlling the electronic properties of graphene involves the introduction of heteroatoms in the lattice structure, which offers a practical method for controlling their properties by creating new states that modify the electronic

structure of graphene. In recent years, many efforts have been focused on synthesizing and characterizing boron and nitrogen-containing single layer graphene, because they are the nearest neighbors to carbon in the periodic table that can provide *p*- and *n*-doping, respectively [5–10].

Phosphorous has also been targeted as a viable dopant candidate for a wide range of applications for nanostructured carbon materials. The high oxidation potential of the P-doped nanotubes makes them good candidates for electrode materials in fuel cells and metal-free catalysts [11,12]. The chemical reactivity of P-doped carbon nanostructures also makes them promising as gas sensors with improved sensitivity [13]. However, the introduction of phosphorus atoms in the sp^2 framework has proven challenging because they have a larger radius than the carbon atom and therefore cannot maintain the planar structure of the graphene lattice [14–16]. Extensive theoretical studies have been performed

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for phosphorous-doped graphene, been discovered that the presence of P atoms in the lattice displaces the positions of the first-, second-, and third neighbors in the plane [17]. These topological defects introduced in phosphorous-doped graphene can cause an important decrease in the carrier mobility. However, phosphorous atoms exhibit donor ability much higher than nitrogen. Therefore, phosphorus doping in graphene is expected to produce a much stronger effect than nitrogen doping. Recently, phosphorous-doped graphene field-effect transistors were produced with a promising performance [18]. There are only few reports on phosphorus doping of exfoliated graphene or graphene oxide in the literature [19–22], and there are no reports on the incorporation of phosphorus during graphene growth.

The use of chemical vapor deposition (CVD) is an established low-cost route for synthesizing large area high quality graphene in the presence of a transition-metal catalyst and a carbon-containing precursor [23]. In this work, the growth of single-layer graphene using a low-pressure CVD system and triphenylphosphine as a precursor is reported. X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the possible phosphorus incorporation into graphene and different chemical environments involving phosphorous atoms. The results of Raman spectroscopy measurements indicated that the graphene degradation increased as the amount of triphenylphosphine increased. In addition, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed the formation of nanostructures on top of the graphene layer, the number of these nanostructures was directly related to the amount of precursor used for sample growth.

2. Materials and methods

Graphene sheets were synthesized in a high vacuum low-pressure CVD system, using triphenylphosphine ($\text{P}(\text{C}_6\text{H}_5)_3$) as precursor and 25 μm -thick copper foils (99.8% pure) as the catalyst. Both materials were provided by Sigma Aldrich. The base pressure of the system was around 0.1 mTorr, which was achieved by a turbo molecular pump coupled to a 1-inch quartz tube placed inside a one stage tubular furnace. The solid precursor was loaded into a small quartz tube and placed at the gas flux just prior to the entrance of the furnace. The copper foils were annealed to 1000 °C under a 2-sccm H_2 flux for 20 min. The precursor was subsequently heated to vaporization while the catalyst under the hydrogen flux were kept at 1000 °C. Processing temperatures of 900 °C and 950 °C were also tried. Triphenylphosphine maximum vapor pressure was 5 mTorr and growth time was approximately 10–15 min. Four cases were studied corresponding of a precursor mass of 10, 20, 30 and 40 mg. The partial pressure of hydrogen during all growths was 65 mTorr. The obtained sheets were transferred onto SiO_2/Si wafers using a wet transfer method. A support layer of polymethylmethacrylate (PMMA) solution in anisole was spin-coated onto the graphene/copper surface and an iron chloride solution was used to dissolve the copper foil. The PMMA/graphene/ SiO_2 stack was heated at 60 °C for 10 min to improve bonding between graphene and the substrate. The PMMA was removed with acetone.

The samples were characterized using a multitechnique approach. Raman spectroscopy was performed using a micro-Raman spectrometer (NT-MDT, NTEGRA SPECTRA) equipped with a CCD detector and a solid-state laser, which produced an excitation wavelength of 473 nm. Care was taken to avoid sample damage and several measurements were performed at different laser power to discard any band dispersion effect caused by laser-induced heating. Measurements were performed using a 100 \times objective giving a laser spot of the order of 1 μm with an incident power of less than 0.2 mW. The spectrometer is equipped with a piezoelectric stage

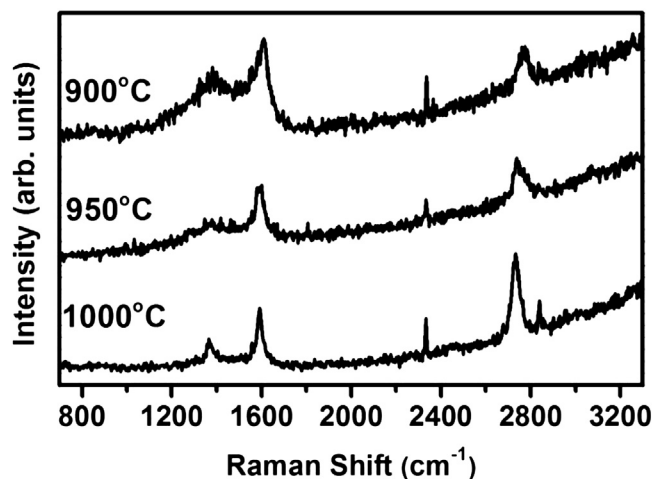


Fig. 1. Raman spectra obtained from samples on copper foils prepared with 20 mg of triphenylphosphine at different temperatures (laser wavelength was 473 nm).

that allows for Raman mapping.

A field emission scanning electron microscope (FEG-SEM, JSM-6701F, from JEOL) operating at 1 kV and a field emission transmission electron microscope (FEG-TEM, JEM-2100, from JEOL) operating at 100 kV and equipped with a CCD camera (11 M pixel GATAN Orius Camera) were employed for electron microscopy analysis. Both microscopes are equipped with energy dispersive spectroscopy (EDS) analysis system. The samples were transferred onto a holey carbon grid for TEM observation using the same procedure adopted for graphene transfer to oxidized silicon wafers.

X-ray photoelectron spectrometry (XPS) was performed using an Mg $K\alpha$ x-ray source ($h\nu = 1253.6$ eV) and an Alpha 110 commercial hemispherical electron energy analyzer. The XPS spectra were collected at a fixed analyzer pass energy of 20 eV, and the data were processed using the CasaXPS software.

3. Results and discussion

The Raman spectra obtained from samples grown using 20 mg of the precursor material at temperatures in the 900 °C–1000 °C range are shown in Fig. 1. The measurements were performed prior to being transferred to an oxidized silicon wafer. The spectra clearly indicated that graphene was only obtained at the highest temperature. The other spectra indicated the presence of an important

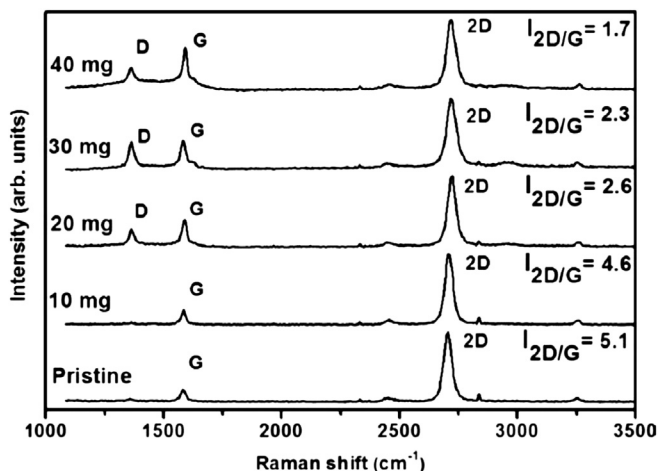


Fig. 2. Raman spectra of samples obtained after transferring the graphene to the oxidized silicon surfaces and grown using different amounts of precursor.

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