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Taguchi optimized synthesis of graphene films by copper catalyzed ethanol decomposition ☆

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ABSTRACT

Taguchi method is for the *first time* applied to optimize the synthesis of graphene films by copper-catalyzed decomposition of ethanol. In order to find the most appropriate experimental conditions for the realization of thin high-grade films, six experiments suitably designed and performed. The influence of temperature (1000–1070 °C) and synthesis duration (1–30 min) and hydrogen flow (0–100 sccm) on the number of graphene layers and defect density in the graphitic lattice was ranked by monitoring the intensity of the 2D- and D-bands relative to the G-band in the Raman spectra. After critical examination and adjusting of the conditions predicted to give optimal results, a continuous film consisting of 2–4 nearly defect-free graphene layers was obtained.

1. Introduction

The outstanding properties of graphene make it attractive for applications in very different fields [1–5]. Graphene is successfully obtained by different techniques, such as exfoliation of graphite [6] and epitaxial growth [7]. Nonetheless, chemical vapor deposition (CVD) is presently the preferred method for the synthesis of large-area graphene films with high spatial uniformity [8,9]. For this kind of deposition a transition metal (commonly nickel or copper) is used as substrate to catalyze the decomposition of a hydrocarbon gas (most frequently methane). Recently, ethanol (C_2H_5OH) has also been tested as carbon precursor for graphene synthesis [10,11], obtaining large area, continuous films with comparable quality to those synthesized by methane. The interest in using ethanol lies primarily in its safety, low cost, and easy handling. In catalytic CVD, hydrogen is known to influence the morphology of the carbons [12]; for example, it can allow the formation of open forms of carbon, such as graphite platelets, by stabilizing their growing edges. However, its role in the graphene synthesis has not been completely clarified yet. Overall, the fabrication of thin, high-grade films of graphene calls for the optimization of the synthesis process.

In this work, the synthesis of graphene films by copper-catalyzed growth from ethanol precursor at high temperature (1000–1070 °C) is considered, and the effect of CVD duration (1–30 min) and hydrogen flow (0–100 sccm) is investigated.

Taguchi method is a powerful and efficient tool extensively applied to the optimization of multifactor processes in very different fields [13–22]. It consists in an empirical approach, which combines mathematical and statistical techniques and utilizes orthogonal arrays (OAs) to study a large number of variables with a small number of trials [13]. OAs are subsets of the full factorial experiment (involving L^F trials, where F is the number of factors investigated at L levels). In OAs each variable setting occurs at an equal number of times and none of two settings are the same, so that the resulting experiments are balanced and the effect of each factor under study can be discriminated from the effect of other factors (i.e. interactions between parameters are neglected).

Taguchi approach proceeds through 1) selection of the parameters (control factors) governing the considered process and choice of their levels; 2) design of experiments to be performed to investigate the parameters' influence on the process, i.e. adoption of the most suited (to number of factors and levels) OA; 3) running of the planned experiments; 4) analysis of the process response in terms of the selected outputs; and 5) running of new experiments to test the configurations under which the process is predicted to give optimal responses. Currently, this procedure is employed in a large number of diverse fields, ranging from electronics [13,14] to robotics [15], and from medicine [16] to material science [17–22]. In the latter case, its application is

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often addressed at optimizing the production of materials in different forms, such as diamond-like carbons [17] and polycrystalline diamond [18] coatings, silver [20] and zinc oxide [19] nano-sized particles, carbon nanotubes [22] and related hybrid nanostructures [21].

Here, Taguchi method is for the *first time* utilized to optimize the synthesis of graphene and to find the most suitable experimental conditions for the production of highly crystalline thin films by copper-catalyzed decomposition of ethanol. In order to monitor the results of CVD experiments, the graphene films are systematically investigated by high-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) and micro-Raman spectroscopy (MRS).

2. Experimental details

2.1. Design of experiments

Table 1 shows control factors and levels selected to perform the CVD growth experiments. Two alternative levels for the synthesis temperature (T_S), 1000 °C and 1070 °C, are chosen. Hydrogen flow (Φ_{H2}) and synthesis duration (t_S) are allowed to assume three levels in the ranges 0–100 sccm and 1–30 min, respectively. Since a process ruled by one two-level and two three-level factors has $1 \cdot (2-1) + 2 \cdot (3-1) + 1 = 6$ freedom degrees [23], an OA is selected which allows investigating the effect of T_S, Φ_{H2} and t_S (neglecting the mutual factor-interactions [21]) by performing only 6 experiments in place of 18 (i.e. $2^1 \cdot 3^2$, as in principle required by traditional methods). The corresponding design of experiments (DOE) is reported in Table 2. The samples obtained under DOE experimental settings are labeled as D*N* with *N* a number running from 1 to 6.

2.2. Film growth

The experimental setup utilized for the synthesis consists of a thermal reactor with fast cooling system (implemented at ENEA laboratories). 25 μm thick copper foils (PHC Se-Cu58, 99.95 purity) are used as growth substrates. Once placed into the reaction chamber, with pressure stabilized at 4 mbar, the substrates are annealed for 20 min at T_S under a 40 sccm flow of Ar/H_2 (1:1 mixture). After annealing, Φ_{H2} is set to the selected value and the synthesis is performed using argon as carrier gas (20 sccm) and ethanol (0.1% of Ar flow) as carbon source. After a time t_S, the samples are extracted from the hot zone, let to cool to near room temperature (RT), and then extracted from the vacuum vessel. The copper is fully etched via a diluted nitric acid bath (HNO_3 70% in H_2O, 1:3) for 2 h at RT; after that time, the free floating carbon film is scooped from the solution with thermally oxidized silicon wafer and transferred into distilled water for removal of acid bath residues. Finally, the graphene film is scooped from water and it is thus ready to be analyzed.

2.3. Film characterization

The morphology of the deposited films is evaluated by means of HRTEM (Tecnai F20, operated at 120 kV to reduce radiation damage to graphene crystals) and AFM (Bruker Dimension Icon SPM).

Raman scattering is measured in air at RT with an Instrument S.A. Ramanor U1000 double monochromator, equipped with an Olympus BX40 microscope for micro-Raman sampling and with an electrically cooled Hamamatsu R943-02 photomultiplier for photon-counting detection. The 514.5 nm (2.41 eV) line of a Coherent Innova 70 Ar^+ ion laser is used as an excitation source. The 1200–2850 cm^{-1} spectral range is analyzed. A X100 objective focuses the laser spot to a diameter of approximately 1 μm. Care is taken to minimize heating or damage to the sample by choosing low laser power (below 1 mW at its surface). Three different locations are sampled in order to reliably describe each specimen and discard possible spatial in-homogeneities. An acquisition time of 15 s is used to obtain a sufficient S/N ratio. Spectra are averaged, normalized and analyzed using a commercially available spectroscopic analysis software package. Lorentzian bands, superimposed to a constant background, are used to fit the spectra.

Further technical details, concerning measurements performed and instrumentation utilized, can be found elsewhere [24].

Table 1
Control-factors and levels selected to perform Taguchi-designed CVD growth experiments.

Control-factors	Levels		
	1	2	3
T_S (°C)	1000	1070	
Φ_{H2} (sccm)	0	10	100
t_S (min)	1	10	30

Table 2
Taguchi-design of experiments for CVD process.

Experiments[a]	Control factors		
	T_S (°C)	Φ_{H2} (sccm)	t_S (min)
D1	1000	0	1
D2	1000	10	10
D3	1000	100	30
D4	1070	0	10
D5	1070	10	30
D6	1070	100	1

[a] Argon (20 sccm) and ethanol (0.1% of Ar flow) are used as a carrier gas and a carbon source, respectively.

3. Results and discussion

3.1. Properties of the deposited films

The most prominent features in the Raman spectra of graphene using laser excitation at 2.41 eV are the G peak appearing at 1582 cm^{-1} and the G′ peak at about 2700 cm^{-1}. In the case of disordered samples, or at the sample edges, the disorder-induced D-peak is also detected around 1350 cm^{-1}. The G peak, associated with the doubly degenerate iTO and LO phonon mode (E_{2g} symmetry) at the Brillouin zone center, is the only peak coming from a first order Raman scattering process in graphene [25]. The G′- and D-peaks originate from a second-order process, involving two iTO phonons near the K point for the G′ band, or one iTO phonon and one defect in the case of the D-peak [25]. The G′ peak is often termed as the 2D peak since its frequency is approximately twice the D peak frequency.

The D to G relative intensity (I_D/I_G) commonly monitors the density of lattice defects in nanocarbons [25]. Information about the number of graphene layers (n_{GL}) can be deduced from shape and relative intensity of the 2D-peak. In graphene produced by micro-mechanical cleavage of bulk graphite, a single Lorentzian component (FWHM ~ 24cm^{-1}) well reproduces the 2D peak of single-layer (1 L) graphene, whereas four Lorentzian components are needed in case of bi-layer (2 L) graphene [25,26]. Raman spectrum of multi-layer (ML) graphene ($n_{GL} > 5$) is hardly distinguishable from that of bulk graphite. In CVD graphene, the shape difference of the 2D-peak for one or more than one layer could be not as clear as in exfoliated graphene, due to the lower electronic coupling between layers with not-ordered stacking. A narrow Lorentzian line (~30–40 cm^{-1}) can be used to fit the 2D-peak of both 1 L and 2 L CVD graphene, while for $n_{GL} \geq 3$ the width of 2D (Lorentzian) peak increase up to ~70 cm^{-1}. The 2D to G intensity ratio (I_{2D}/I_G) is used as a qualitative parameter to evidence the presence of very few graphene layers, being in this case $I_{2D}/I_G > 1$ [25].

Results of Raman scattering measurements on films deposited under the conditions reported in Table 2 are shown in Fig. 1. In order to