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Contact Angle Influence on Defects in Graphene Prepared by Segregation Method on Treated SiO_2/Si Substrates

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Abstract

SiO_2/Si substrates were modified by physical and chemical treatments in order to improve adhesion and homogeneity of segregated graphene. The objective of this work was to decrease defects concentration in graphene crystallites in segregated graphene. It was done by chemical and physical treatment of the SiO_2 substrate prior to deposition of catalytic nickel layer. By the experiments, it was shown that concentration of defects in graphene strongly increases with increasing contact angle. Graphene with lowest I_D/I_G ratio of Raman bands D and G, therefore highest quality, was prepared on substrates annealed in reduction atmosphere.

Keywords: Graphene; Silicon dioxide; Contact angle

Introduction

Graphene is a constant subject of studies of scientific teams due to numerous outstanding properties. Despite the large quantity of publications covering area of graphene research and preparation, graphene is still one of the materials requiring attention. There is many proposed applications in various fields, therefore new preparation methods are still being developed and partial problems are being described [1].

Frequently used methods of graphene preparation are so-called transfer-free methods [2-4]. These methods utilize metallization deposited on a dielectric substrate. The metallization contains carbon in various forms, which serves as a source for graphene formation. The metallization further contains catalytic metal, which ensures formation of the crystalline graphene film on the surface of the dielectric layer during the process of annealing and consequent cooling of the structure. An essential step of the preparation process is etching-off of the metallization. This way the structure of graphene/dielectric is directly obtained without the necessity to transfer prepared graphene layer onto a dielectric substrate. The resulting structure can be then used for several applications. In our work, we focused on the preparation of graphene from the structure C/Ni/SiO_2/Si. The scheme of the graphene preparation process is on Figure 1:

- Nickel deposition onto treated SiO_2 / Si substrate by e-gun evaporation,
- Carbon deposition by flesh evaporation,
- Annealing and subsequent cooling,
- Etching of the metallization.

The objective of this work was to decrease defect concentration in graphene crystallites in segregated graphene. It was done by various types of treatment applied to the SiO_2 substrate prior to deposition of catalytic nickel layer. We find out that the concentration of these defects depends on the contact angle of the SiO_2/Si substrate after the chemical treatment. Characterization of the samples was done by contact angle measurement and by Raman spectroscopy; evaluation of the graphene defect concentration was based on the Pimenta et al. procedure [5].

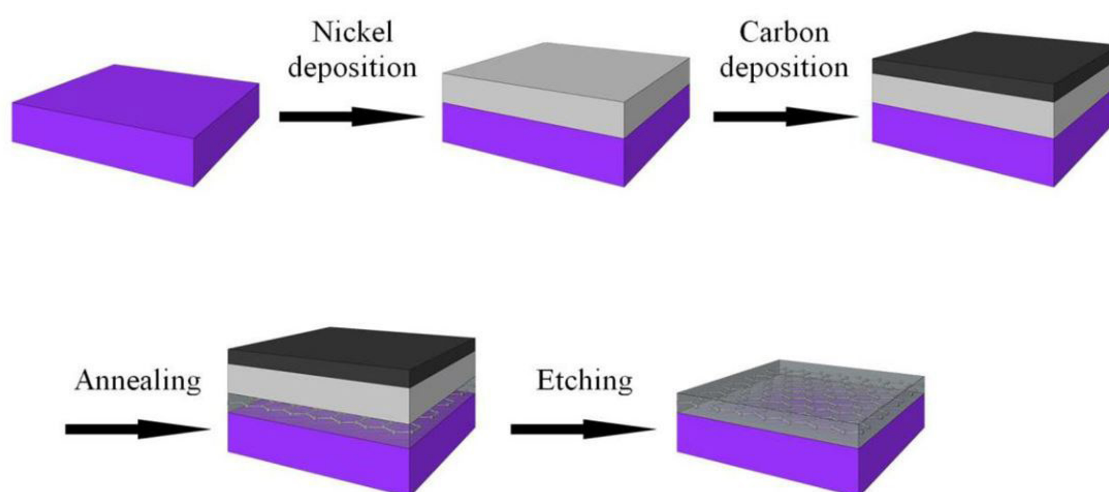

Figure 1: Scheme of the graphene preparation process

Experimental

The substrate for graphene formation was a 300 nm thick SiO_2 layer, prepared by thermic oxidation – this structure had been purchased from ON Semiconductor, Rožnov p. Radhošťem, Czech Republic.

Target substrates were investigated by atomic force microscopy (Dimension ICON, Bruker Corp.) in ScanAsyst mode. Silicon Tip on Nitride Lever SCANASYST-AIR with spring constant 0.4 N/m was used, NanoScope Analysis software was applied for data processing. The mean roughness Ra of measured substrates was 0.16nm, AFM scan can be seen in Figure 2.
Prior to metal deposition, the SiO_2 plates were cleaned using these processes:

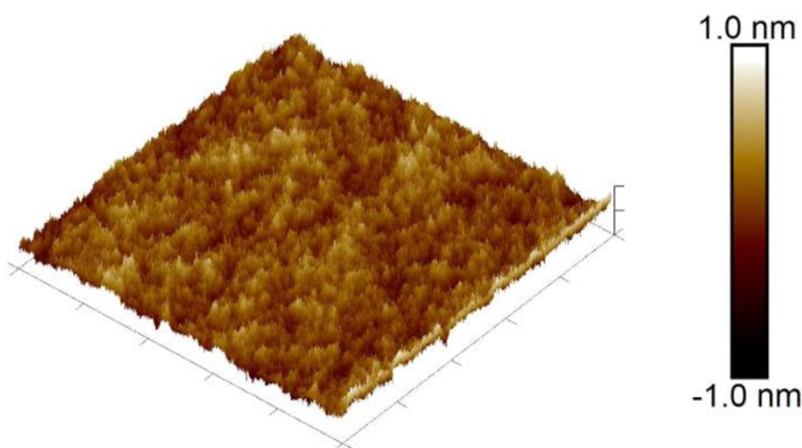

Figure 2: AFM scan of the surface of SiO_2/Si substrate after standard cleaning with roughness Ra of 0.16nm. The mean roughness values (Ra) represent the average of the deviations from the centre plane of the sample

• Standard (reference) process – acetone bath in ultrasonic cleaner for 5 minutes, then 5 minutes in isopropyl alcohol (IPA). After removal, substrates were dried with nitrogen flow and put directly into chamber for nickel evaporation.

• Chemical cleaning – after the standard process, 24-hour bath with different chemicals (toluene, isobuthylmethylketone (IBMK), chloroform, hexane, sulphuric acid, nitric acid). Temperature was 20 °C. After removal, substrates were rinsed by acetone and IPA and dried with nitrogen flow.

• Annealing in reduction atmosphere – substrates were annealed for 2 hours in mixture of argon and hydrogen (Ar:H2 95:5), annealing temperature 850 °C, Pressure 110 kPa.

• Plasma treatment – substrates were put in the plasma chamber and oxygen plasma was applied, pressure in the chamber was $1x10^1$ Pa, voltage 1 kV, current 60 mA, duration10 minutes.

Contact angles (CA) on modified substrates were measured within 10 minutes after the modification process by sessile drop method. Measurements were performed on KRŰSS DSA 100 equipment using distilled water. Temperature during the measurement was 20 °C. Deposition of the 2 μl droplet was performed at a rate of 0.16 ml / min. On each substrate, contact angle was measured 20 times, every time on different spot.

100nm-thick nickel layer was deposited using e-gun evaporation in vacuum chamber at 2 x 10^{-4} Pa (apparatus UNIVEX 450). Rate of deposition was kept constant at 0.01 nm/s.

The amorphous carbon was sputtered using flash evaporation of woven carbon fibre thread (apparatus: BAL-TEC SCD 050). Distance between carbon thread and substrate was 5cm. The chamber was evacuated up to 30 Pa, then rinsed 3 times with Argon gas, then degassing was performed with current of 1.2 A. The Chamber was once again rinsed with Ar and after evacuation current of about 20 A was applied until the carbon thread exploded (thickness of C was approximately 20 nm).

Annealing process was done in a small vacuum chamber equipped with a resistively heated ceramic boat Boralectric Heating Element HTR-1001 at 850 °C and 3 x 10^{-4} Pa. Samples were annealed for 2 hours.

Raman analysis was carried out using the Thermo Scientific DXR Raman Microscope spectrometer equipped with confocal Olympus microscope, Nd: YAG laser - λ=532 nm, laser power = 7 mW. Omnic software was used for evaluation of received Raman spectra.

We chose mixture of acids (acetic, sulphuric and nitric acid) together with distilled water in ratio 10:4:10:200 for etching the metallization. During the etching process samples were observed under optical microscope. Final etching time was 75 minutes under ambient conditions.

Chemical treatment	**Contact angle (°)**
Reference process	**72.29**
Hexane	41.44
Chloroform	41.32
IBMK	40.00
Toluene	37.23
Sulphuric acid	30.91
Nitric acid	30.65
Oxygen plasma	18.48
Reduction atmosphere	12.96

Table 1: Corresponding contact angle measured on chemically treated substrates

Results and Discussion

The purpose of the experiments was to observe, whether chemical treatment of given substrate affects resulting quality of segregated graphene. We chose firstly different organic solvents to see if there would be any differences in CA since there can be residues after the cleaning procedure. These residues may differ and therefore the CA would differ as well. Later on we implemented etching of substrates by sulphuric and nitric acids with a vision of removing top layers of silica to make the substrate clean as much as possible. Etching with oxygen plasma tends to be more consistent in removing top layers of silica and that is why it was used as well, promising to keep substrate as smooth as possible. Annealing substrates in H2 atmosphere was different approach. We chose this treatment to see, if we can adjust the chemistry of silica layer in contrast to oxygen-rich silica prepared by O_2-plasma treatment. In order to quantify the effect of substrate treatment CA was measured right after the treatment procedure. The time gap between the removal from the bath and measurement was less than 10 minutes. Results of CA measurements are in Table 1, where 1st column contains type of treatment and 2nd column contains statistically processed value of CA. Highest value of CA was measured on substrates without treatment (reference), the lowest contact angle value corresponds to substrate annealed in reduction atmosphere. Etching in sulphuric and nitric acid resulted in approximately same CA value. Chemical treatment in organic solvents led to the decrease of CA to approximately 40°.

Chemically treated substrates were used for preparation of segregated graphene layer. As previously described, graphene was analysed via Raman Spectroscopy. Examples of measured Raman spectra can be seen on Figure 3. These 3 spectra correspond to 3 processes; one spectrum is reference (black), second stands for treatment in chloroform (blue) and third corresponds to annealing in reduction atmosphere (red). At the preparation conditions, that we used few-layer graphene was prepared being composed of 4-5 layers on average [5]. Our attention was paid towards concentration of microscopic defects, which is expressed by ratio of intensities of D-band and G-band of Raman spectra, I_D/I_G. In Figure 2 one can see that while the intensity of G-band remains the same, D-band intensity varies a lot. That results in a notable difference of I_D/I_G. Because of that we show dependency of I_D/I_G on CA in Figure 4, where there is a observable increasing tendency of defect concentration with increasing CA. Graphene with the lowest I_D/I_G, therefore the highest quality, was prepared on substrates annealed in reduction atmosphere. On these substrates, we measured very low value of I_D/I_G (0.12). On the other hand, highest I_D/I_G (0.88) was measured on reference samples with no treatment. Interesting results are also values of I_D/I_G measured on substrates previously etched with nitric and sulphuric acid. These values are 0.48 and 0.43 respectively. It is obvious that these two values are very close to each other as well as the CA values. Good quality graphene was also obtained using substrate treated with oxygen plasma.We used logarithmic function to estimate

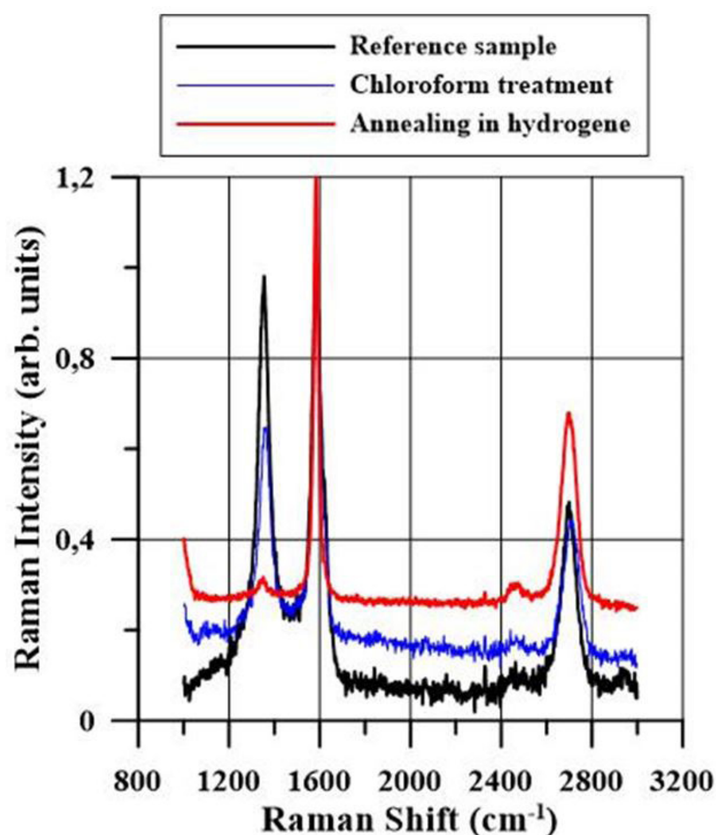

Figure 3: Raman spectra measured on chemically treated substrates

I_D/I_G dependency on CA. For our fitting curve regression coefficient R2 was found to be 0.82. Obviously, such a low value of R2 is caused by experimental data for CA around 40°, where experimental points strongly mismatch with fitting curve. All these points correspond to the treatments with organic solvents. We think that this low reproducibility can be caused by imperfect removal of the solvent. These residues would be covered with nickel and during the annealing process; they would expand resulting in defects of nickel barrier. This mechanism could explain higher defect concentration and also lower reproducibility and therefore it would explain deviations of experimental data shown on Figure 4.

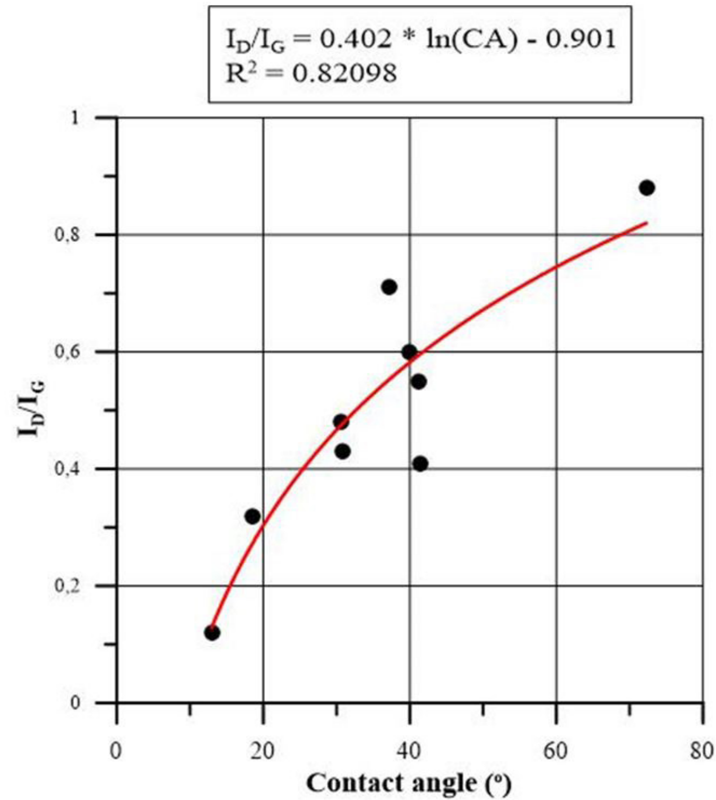

Figure 4: Defect concentration (I_D/I_G) as a function of contact angle (corresponding to different treatment methods)

Conclusion

SiO_2 / Si substrates were modified by physical and chemical treatments in order to improve adhesion and homogeneity of segregated graphene. On modified substrates, we prepared few-layer graphene films and characterized them with Raman spectroscopy. It was shown that concentration of defects in graphene strongly increases with increasing CA. Graphene with lowest I_D/I_G, therefore highest quality, was prepared on substrates annealed in reduction atmosphere. Meanwhile it was shown that CA does not affect number of segregated layers.

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