

Laser-induced modification of graphene in the presence of ethanol on a graphene–substrate interface

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Abstract. We have studied the effect that the substitution of an organic substance (ethanol) for water adsorbate on a CVD graphene–SiO₂/Si interface has on the laser-induced modification of graphene and graphene structures on the SiO₂ film. Scanning probe microscopy has been used to analyse changes in the electronic properties of graphene structures on a hydrophilic substrate in the presence of ethanol and as a result of a laser-induced spatial redistribution of a water–alcohol adsorbate on the interface. It has been demonstrated experimentally that ethanol substitution for water adsorbate leads to an increase in the surface potential of the graphene, which is equivalent to a reduction in its work function with respect to the original level under normal conditions at a relative humidity of air from 30% to 60%. In the laser irradiation zone, we observe an additional increase in surface potential by 30–50 mV. Thus, ethanol makes it possible to tune the laser-induced electronic properties of graphene on a substrate. In addition, it has been shown that the intercalation of ethanol molecules leads to severe temporal instability of the physical properties of graphene structures produced by local laser irradiation. We have demonstrated the possibility of information ‘rewriting’ by low-intensity laser pulses in microregions with a changed surface potential in the presence of ethanol.

Keywords: graphene, water adsorbate, ethanol, laser irradiation, electronic properties of graphene.

1. Introduction

The sensitivity of many physical properties of graphene to the presence of adsorbate molecules on its surface appears to be a significant physical effect involving this new carbon nanomaterial. Experimental and theoretical first-principles studies have shown that the dipole mechanism underlying the effect of adsorbates – both inorganic (e.g. water and nitrogen dioxide) and organic (acetone, dichloromethane, ethanol, hexane and toluene) – on graphene causes changes in its electronic properties [1, 2].

Water adsorbate plays a special role in this context. In many cases, a graphene sheet is transferred to a hydrophilic substrate and studied under atmospheric conditions. As a

consequence, water adsorbate is present on the outer surface of the graphene sheet. More importantly, graphene samples inevitably (and uncontrollably) contain water adsorbate on the graphene–substrate interface. This causes interesting effects. In particular, as shown earlier [3–5] exposure of graphene to multiple low-intensity nanosecond focused laser pulses at a wavelength $\lambda = 0.53 \mu\text{m}$ to a fluence $F \approx 0.04\text{--}0.08 \text{ J cm}^{-2}$ (the laser ablation threshold for graphene being $\sim 0.25 \text{ J cm}^{-2}$) produces local changes in its surface topography. The laser-modified zone has microdepressions up to 2 nm in depth (nanopits), where the mechanical and electronic properties of the graphene (its work function and electrical conductivity) differ markedly from those of the unirradiated material. One possible reason for the formation of micropits (craters) is the local heating of the water adsorbate on the graphene–substrate interface by laser pulses and the displacement of the forming water vapour to the periphery of the irradiated zone, which leads to a decrease in the thickness of the water adsorbate under the pit. The work function of graphene was shown to be directly related to the thickness of the water adsorbate layer on the graphene–substrate interface [6, 7]: the thinner the adsorbate layer, the lower the work function. Bollmann et al. [7] attributed the observed changes in the electronic properties of graphene to the presence of a water layer on the graphene–substrate interface, because such a layer effectively shields the surface charge on the electrically insulating substrate. According to density functional theory calculations [7], the largest increase in the work function of graphene is produced by two or three water monolayers on its surface. Remarkably, the nanopits produced in our experiments are stable over time (the geometry and electronic properties of the modified material remain unchanged). There is also evidence that a reduced work function can be reversibly written in particular graphene areas owing to the local water adsorbate redistribution over the graphene–substrate interface when the surface areas adjacent to the crater are reirradiated, which means that there is a real basis for producing arrays of reversible optical memory elements [4, 5].

The objectives of this work are to examine the feasibility of removing the water adsorbate layer from the graphene–substrate interface and replacing it by ethanol and to assess the effect of laser irradiation on such structures. The properties of water–alcohol solutions have been studied in sufficient detail. Being a polar liquid, ethanol can essentially completely (up to $\sim 95\%$) dissolve in water, another polar liquid. Ethanol dissolution in water is energetically favourable: mixing ethanol and water is accompanied by heat release, indicative of an exothermic reaction, and a reduction in the volume of the components (so-called contraction). Water and ethanol in solution are in a more dissociated state than they are in pure

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form at the same temperature. The above strongly suggests that ethanol is capable of effectively replacing the water adsorbate on a graphene–substrate interface.

2. Experimental

The samples used in our experiments had the form of polycrystalline graphene sheets grown by chemical vapour deposition (CVD) on copper foil and then transferred to a SiO_2/Si substrate. The thickness of the SiO_2 film on the silicon was ~ 300 nm. In the experiments, we used few-layer graphene regions (two to six layers) recovered using micro-Raman spectroscopy. The samples were exposed to 532-nm laser pulses ($N = 10^4$) at particular points on the graphene surface. Note that such laser radiation is negligibly absorbed in water and ethanol. The laser pulse duration was 7 ns and the pulse repetition rate was 1 kHz. The laser beam was focused to a $1/e$ spot diameter of ~ 0.5 μm by the optical system of an Ntegra Spectra M scanning probe microscope (SPM). The laser fluence F was 0.07 – 0.08 J cm^{-2} . In addition, the SPM was employed to examine laser irradiation results using a platinum-coated silicon probe (Pt/Si probe, tip radius of ≈ 30 nm). Surface topography was studied in intermittent contact mode (so-called tapping mode) before and after laser irradiation. Concurrently with surface topography measurements, we recorded the image phase contrast signal, resulting from the phase shift between the probe and master oscillator (for example, due to local changes in the elastic modulus of the surface being tested).

The work function of graphene was assessed by scanning Kelvin force microscopy (SKFM). Using two-pass SKFM, we were able to compare the surface topography to the surface potential distribution. If a Pt/Si probe was used, the spatial resolution of the method was ~ 50 nm and the potential was measured with an accuracy of ~ 1 mV.

Laser irradiation and SPM measurements were performed under atmospheric conditions at room temperature and relative humidity in the range 30% to 60%. Ethanol was delivered to the graphene–substrate interface by merely immersing the sample in ethanol.

3. Laser irradiation in a humid atmosphere and in the presence of ethanol

3.1. Starting sample in a humid atmosphere

Figure 1 shows surface topography, surface potential and phase contrast maps of the starting graphene sample immediately after laser irradiation at 25 points in the scan area (exp#1).

As seen in Fig. 1a, the craters produced by the laser beam are rather difficult to detect against the background of the polycrystalline CVD graphene (with a characteristic crystallite size from 1 to 10 μm), unlike in the case of single-crystal graphene sheets produced by exfoliation [5]. At the same time, the surface potential and phase contrast maps in Figs 1b and 1c make it possible, like in the case of single-crystal graphene, to clearly reveal where the substrate–adsorbate–graphene system was exposed to laser pulses, in spite of the complex surface topography. In the laser irradiation zones, we observed a local increase in surface potential (and accordingly in work function). As shown earlier, this is due to an increase

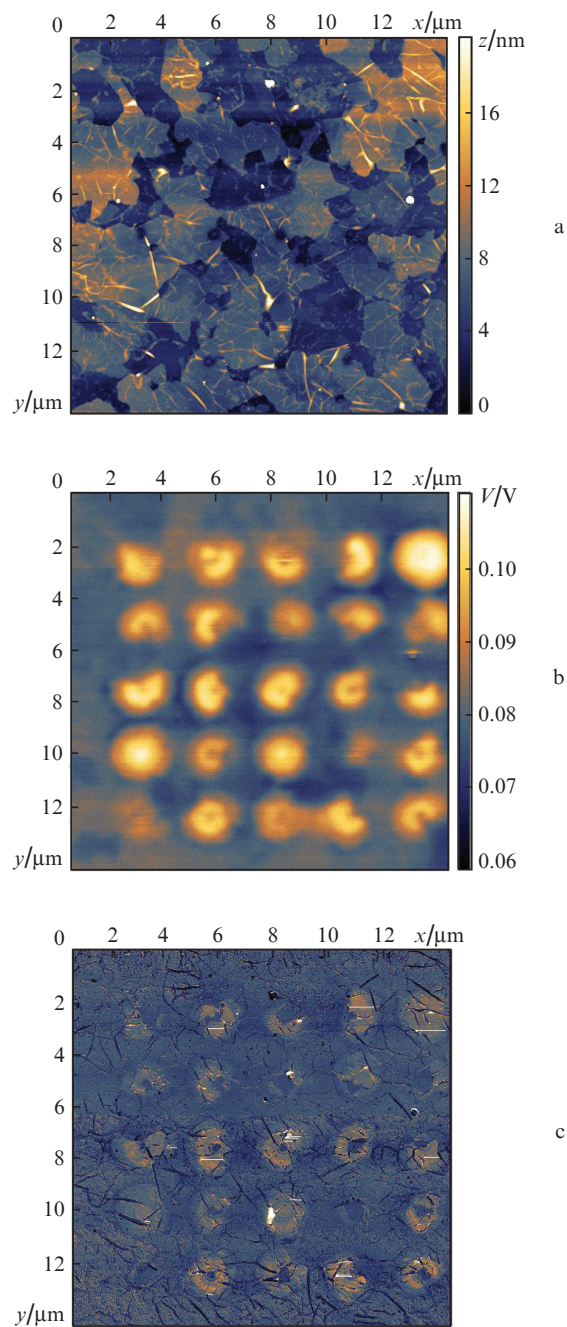


Figure 1. Surface of the starting graphene sample immediately after laser irradiation (exp#1): (a) surface topography, (b) surface potential distribution and (c) phase contrast image. Relative humidity of the air, 60%.

– also local – in the thickness of the water adsorbate layer on the graphene–substrate interface in the laser irradiation zone [5]. The observed distinctions in the potential distribution over the laser irradiation zones are due to the initial thickness nonuniformity of the graphene and, accordingly, of the water adsorbate [6, 7]. The characteristic size of the modified-potential region is comparable to but exceeds the laser spot size (~ 0.5 μm). The phase contrast image demonstrates an increase in the hardness of the graphene structure in the beam waist region owing to the displacement of water layers, whereas in the peripheral parts of this region we observe a decrease in hardness due to the accumulation of the displaced

water adsorbate [4]. These changes in the properties of the graphene structure are stable over time (for at least a week under normal conditions).

3.2. Sample held in ethanol

An unirradiated sample was immersed in ethanol for two weeks. This led to an increase in the average surface potential of the sample by about 50 mV (which corresponds to a reduction in work function by 50 meV) relative to its initial level under normal conditions. Next, the sample was also irradiated. Figure 2 shows the surface potential distributions of the

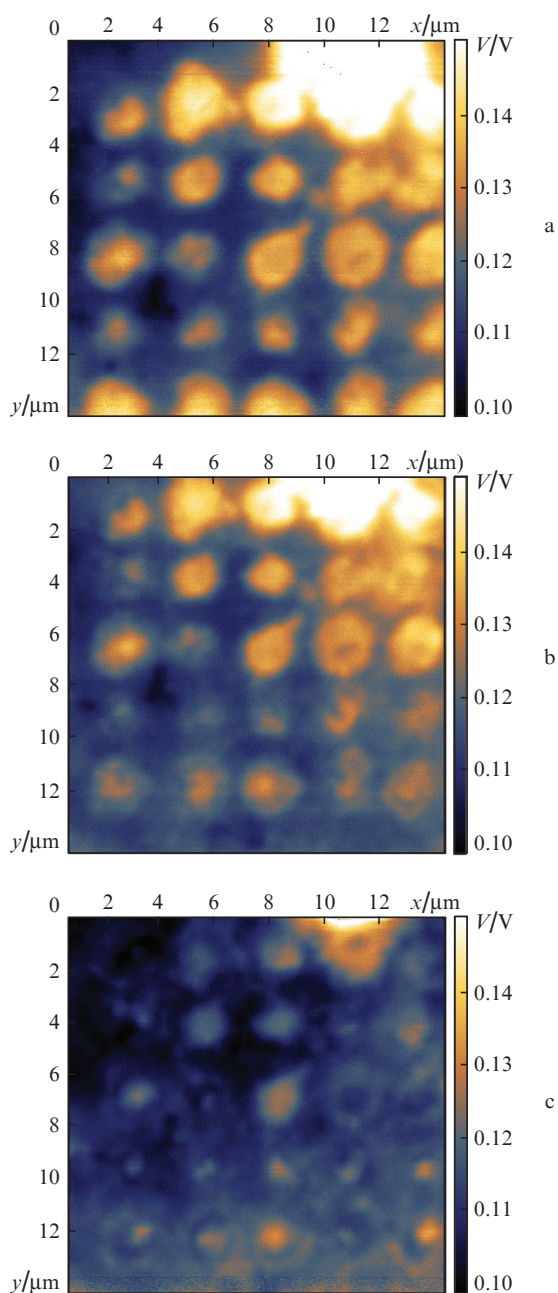


Figure 2. Surface potential distributions of the sample held in ethanol for two weeks and then exposed to laser pulses: (a) immediately after the laser irradiation, (b) 2 h of ‘drying’ in air after the irradiation and (c) 24 h of ‘drying’ in air. Relative humidity of the air, 60%.

sample immediately (Fig. 2a, exp#2), 2 h (Fig. 2b, exp#3) and 24 h (Fig. 2c, exp#4) after the laser irradiation.

After holding in ethanol for two weeks, the graphene surface exposed to laser pulses readily experienced local transformations, resulting in the formation of nanopits up to 2 nm in depth (rather poorly distinguishable against the background of the polycrystalline structure of the graphene sample), and local changes in its electronic properties (increase in surface potential). Note that the laser-induced changes were far less stable over time than those in the case of the starting graphene structures: after just 24 h of air ‘drying’ of the sample held in ethanol, the surface potential of most of the laser-modified zones was essentially equal to that of the unirradiated surface (Fig. 2).

Figure 3 compares a surface potential profile obtained immediately after laser irradiation of the sample held in ethanol (exp#2, grey line) and a profile of the starting graphene sample immediately after irradiation (exp#1, black line) (which corresponds to the surface potential distribution in Fig. 1b). It is seen that the characteristic size of the regions where the surface potential was changed by irradiation is similar to the spacing between the laser irradiation zones, which was 3 μm. Figure 3 clearly illustrates the above-mentioned marked increase (by more than 40 mV) in the general level of the surface potential, undisturbed by laser irradiation, in the presence of ethanol and the slight reduction in the amplitude of the laser-induced local changes in the potential.

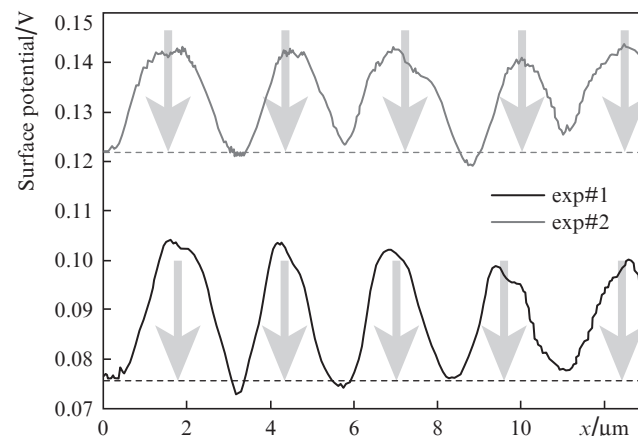


Figure 3. Surface potential profiles of the starting graphene sample (black solid line) and the sample held in ethanol after exposure to laser pulses (grey solid line). The dashed lines represent the average surface potential levels of the two samples before laser irradiation. The arrows indicate the laser irradiation zones on the surface of the samples.

The changes in the surface potential distribution inside and outside the laser irradiation zones can be interpreted as evidence of ethanol substitution for water molecules on the graphene–substrate interface, a slow redistribution of the water–alcohol adsorbate during ‘drying’ under normal conditions and possible restoration of the water adsorbate layer, because during laser irradiation the sample was located in air under normal conditions with RH = 60%.

3.3. Resoaking of the sample in ethanol

The sample held in ethanol was then again immersed in ethanol for another two weeks (the total thus amounting to four

weeks) (exp#5). Next, an unirradiated area on its surface was exposed to laser pulses.

Figure 4 shows surface potential profiles measured immediately after pulsed laser irradiation of the graphene sample resoaked in ethanol (grey line, exp#5) and the starting sample (black line, exp#1). There are also laser-induced local changes in the properties of the graphene structures, but they are even less pronounced in comparison with the continuing slow rise in the average surface potential level (grey dashed line in Fig. 4) of the unirradiated sample surface (the level increased by an additional 10 mV). This can be interpreted as evidence that the surface potential reached the highest possible level for a given graphene structure as a result of further water adsorbate displacement by ethanol from the interface between the graphene and hydrophilic substrate.

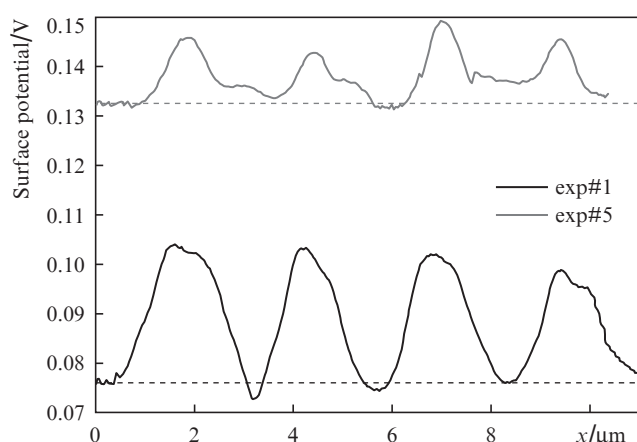


Figure 4. Surface potential profile of the sample resoaked in ethanol for another two weeks and then exposed to laser pulses (exp#5, grey solid line) in comparison with the profile of the graphene sample irradiated without holding in ethanol (exp#1, black solid line). The dashed lines represent the average surface potential levels of the samples before laser irradiation.

4. Discussion of the mechanism underlying the observed effects

Consider in greater detail specific observed changes in the response of the graphene structures to laser irradiation after soaking in ethanol. By way of illustration, the ranges of surface potentials over the entire SPM scan area inside and outside the laser irradiation zones are represented in Fig. 5 by grey and black floating columns, respectively.

First, we discuss the behaviour of graphene outside the laser irradiation zones. There are grounds to believe that the observed increase in the surface potential level of graphene in the unirradiated region by about 50 mV after holding in ethanol (cf. the black exp#1 and exp#2 columns) is due to partial substitution of ethanol molecules for water molecules, resulting in the formation of a water–alcohol mixture on the graphene–substrate interface during the two weeks of holding in ethanol. This is most likely the result of ethanol penetration through defects in the graphene sheet and, to a lesser extent, of the diffusion of ethanol molecules through the graphene lattice, because the size of ethanol molecules is ~ 4 Å and the unit-cell parameter of graphene is 2.5 Å. Concurrently, there is the diffusion of water molecules in the opposite direction:

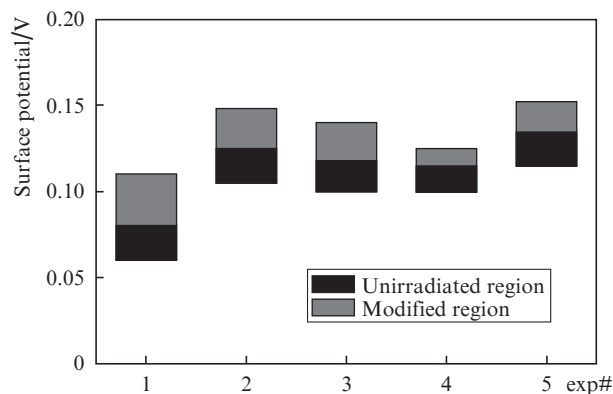


Figure 5. Diagram illustrating the ranges of surface potentials in laser-irradiated (grey columns) and unirradiated (black columns) zones: (exp#1) starting sample immediately after irradiation; (exp#2) sample held in ethanol for 14 days, immediately after irradiation; (exp#3) sample held in ethanol for 14 days, 2 h after irradiation; (exp#4) sample held in ethanol for 14 days, 24 h after irradiation; (exp#5) sample held in ethanol for another two weeks and then again laser-irradiated.

from the graphene–substrate interface to the alcohol solution as an external medium (in particular, possibly through the graphene layer, because the size of water molecules is ~ 3 Å). According to the dipole mechanism of the effect of an adsorbate layer on graphene [7], the observed changes in electronic properties (the higher work function in comparison with ‘perfect’ graphene) are due to the influence of the electric field of the polar adsorbate molecules (both the water and ethanol molecules in our case) on the electronic states of the graphene. The dipole moment of a water molecule is $\mu_w = 1.86$ D and that of an ethanol molecule is slightly lower: $\mu_e = 1.69$ D [8]. Therefore, a water–alcohol mixture generally has a weaker effect on the electronic states of graphene than does a pure water adsorbate, predetermining a higher surface potential (lower work function), of graphene, as observed in experiments. The decrease in the surface potential level of the unirradiated region to about 0.10–0.13 V in 24 h (cf. the black exp#2, exp#3 and exp#4 columns in Fig. 5) attests to the vaporisation of the water–alcohol mixture during ‘drying’ under normal conditions. The surface potential level increases again after holding for another two weeks (exp#5 column), exceeding the level observed after the first holding of the sample in ethanol (exp#2), which points to further displacement of water molecules by ethanol.

Consider now the behaviour of graphene in the laser irradiation zone, in particular, the experimentally observed temporal instability of the surface potential of irradiated regions (grey exp#2, exp#3 and exp#4 columns in Fig. 5). We proceed from the assumption that the mechanism underlying the formation of modified regions – local heating of graphene sheets by laser radiation, accompanied by the formation of adsorbate vapour under the graphene and the displacement of the vapour to the periphery of the laser spot – is operative in the case of a water–alcohol mixture as well. The effect of the laser-induced photovoltage in silicon (Dember effect) on the surface potential can be neglected, because it is of the same order as the thermal potential and the SiO₂ dielectric film is sufficiently thick (~ 300 nm). Thus, one of the factors responsible for the increased surface potential in the modified region compared to the unirradiated graphene surface is the decrease in the thickness of the water–alcohol adsorbate layer

in the laser irradiation zone. Moreover, laser irradiation may change the relationship between the concentrations of the components of the water–alcohol mixture in the irradiated zone, presumably raising the ethanol concentration. With allowance for the overall effect, the change in the surface potential of graphene, ΔV , in the irradiated zone relative to the surface potential level of the platinum coating of the SPM probe (zero level in the diagram) is ~ 0.15 V (see the grey exp#2 column in Fig. 5). The work function of the platinum coating of the SPM probe is $W_{\text{Pt}} \approx 5.3$ eV, so that the minimum work function of the graphene, W_{gr} , observed in these experiments, according to the formula $W_{\text{gr}} = W_{\text{Pt}} - e\Delta V$, is at a level of ~ 5.15 eV. The work function of a ‘perfect’ few-layer graphene, having two to six layers, is near 4.5–4.6 eV [9]. Thus, owing to the combined effect of the above two factors, laser irradiation and holding in ethanol lead to a 12% increase in the work function of the graphene samples relative to that of ‘perfect’ graphene.

As to the temporal instability of the surface potential of the irradiated regions, we propose two alternative hypotheses. Further research is needed to find out which of them better represents the real situation. According to one hypothesis, laser irradiation leads to changes in the concentrations of the components of the mixture in going from the centre of the crater to its periphery. This initiates the osmosis of solvent molecules towards the region with a higher solute concentration from that with a lower solute concentration, i.e. diffusion of water molecules from the periphery to the irradiated zone and that of ethanol molecules from the irradiated zone to the periphery. As a result, the relationship between the components of the mixture in the irradiated zone approaches that in the unirradiated zone with time and returns to its original level before laser irradiation (Fig. 5). The rate of the diffusion process determines the degradation rate of the surface potential of the irradiated regions.

According to the other hypothesis, the temporal instability of the surface potential of the irradiated regions is directly related to the state of aggregation of the adsorbate on the graphene–substrate interface. As pointed out in a number of reports (see e.g. Gowthami et al. [10] and references therein), the molecular layer of the water adsorbate on the graphene– SiO_2/Si interface is in a quasi-solid state, in the form of ice. It is this circumstance which ensures stability of the changes induced in the parent graphene by local laser irradiation. The penetration of ethanol molecules into the graphene–substrate interface and ethanol substitution for water molecules cause the adsorbate to transform into liquid, disturbing the stability of the shape and physical properties of the laser-induced transformations.

5. Erasing the laser-written information on graphene using ethanol

In an additional series of experiments, we performed information ‘rewriting’ on graphene structures. The results are presented in Fig. 6 in the form of a diagram illustrating the ranges of surface potentials in laser-irradiated (grey columns) and unirradiated (black columns) zones: (exp#6) starting sample immediately after irradiation; (exp#7) sample after holding in ethanol for seven days; (exp#8) sample after air ‘drying’ for seven days; (exp#9) sample immediately after a second laser irradiation cycle.

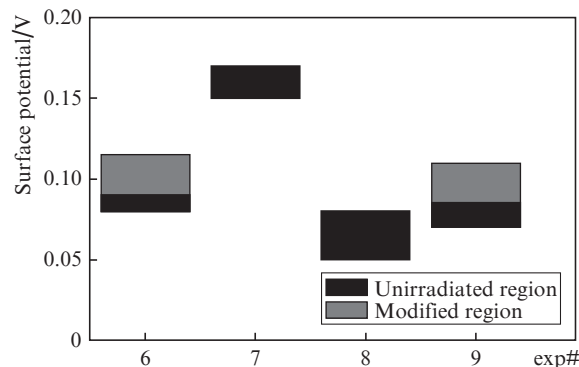


Figure 6. Diagram illustrating the ranges of surface potentials in laser-irradiated (grey columns) and unirradiated (black columns) zones: (exp#6) starting sample immediately after irradiation; (exp#7) sample after holding in ethanol for seven days; (exp#8) sample after air ‘drying’ for seven days; (exp#9) sample immediately after a second laser irradiation cycle.

laser-irradiated. The new array was also characterised by surface potential mapping (exp#9).

Holding in ethanol on the whole increased the surface potential of the graphene (compare the positions of columns exp#6 and exp#7). In addition, it eliminated the nanoparticles on the graphene surface and the potential contrast in the laser-irradiated zone. To better illustrate the changes produced by ethanol intercalation into the graphene–substrate interface, Fig. 7 presents graphene surface height and surface potential

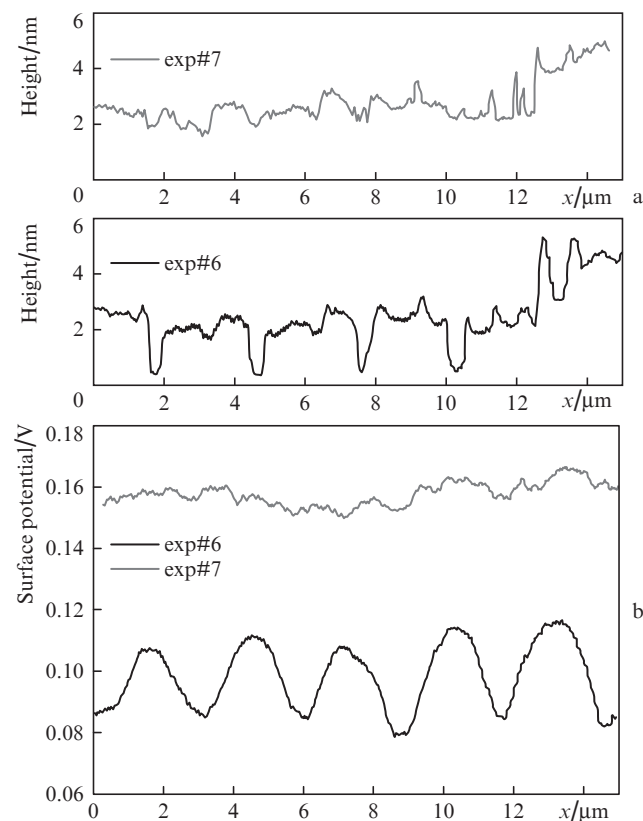


Figure 7. (a) Surface height and (b) surface potential profiles before (black solid lines) and after (grey solid lines) soaking in ethanol.

profiles for one row of the array before (exp#6) and after (exp#7) soaking in ethanol.

Subsequent prolonged (week-long) ‘drying’ of the sample in atmospheric air with RH = 30% reduced the surface potential (Fig. 6, exp#8) as a result of the reverse substitution of water molecules for ethanol. Thus, the described steps allowed us to completely erase the information written on graphene and return the carrier to its original state. The positions of columns exp#8 and exp#9 indicate that the sample retained the ability to store new information. It is worth noting that, when the sample was held in ethanol for a considerably shorter time, information was erased incompletely.

6. Conclusions

The present experimental data on few-layer CVD graphene (two to six layers) demonstrate the possibility of ethanol substitution for water adsorbate intercalated into the graphene–substrate interface and the reverse process: water substitution for the ethanol. The displacement of the water adsorbate by ethanol reduces the work function of the graphene, bringing it closer to the level of ‘perfect’ graphene. The laser-induced local changes in the electronic properties of graphene are shown to depend significantly on the composition of the interfacial adsorbate layer. It is also shown that holding in ethanol may completely eliminate graphene structures produced by laser irradiation in the presence of an intercalated water adsorbate. In combination with the possibility of bringing about the reverse process – water substitution for ethanol – this property enables information to be recorded on a graphene carrier and then erased. Thus, we have proposed and tested a combined method for controlling the electronic properties of graphene structures via a reversible displacement of water adsorbate on the graphene–substrate interface by ethanol in combination with a local adsorbate redistribution on the interface under multipulse laser irradiation.

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