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Pulsed UV-irradiated Graphene Sensors for Ethanol Detection at Room Temperature

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***Abstract*— A graphene-based gas sensor fabricated in a FET (GFET) configuration and its sensitivity towards ethanol and methane is reported. Detection of ethanol at the level of 100 ppm was observed under pulsed UV irradiation and after cleaning by UV light in the N_2 ambient. Reduction of the frequency of UV irradiation pulses resulted in increased changes in sensor resistance in the presence of ethanol. Improved sensing behavior was ascribed to more effective diffusion and adsorption processes at the graphene surface during low-frequency UV light pulses. Additionally, modulation of charge carrier density allowed more pronounced sensor responses at higher gate voltages (~30 V). GFET was insensitive to methane (200 ppm) at room temperature, regardless of irradiation frequency used, suggesting the potential application of selective gas sensing capability of graphene-based devices.**

Keywords—graphene; gas sensor; FET sensor; ethanol detection; pulsed UV; gate voltage.

I. INTRODUCTION

Effective sensing of low concentrations of gases requires novel materials and technologies for selective and fast detection. Graphene and its derivatives are candidates for ultra-sensitive gas sensors due to their highly active surface, ultimate surface-to-volume ratio, and unique charge transfer properties [1], [2]. Molecular adsorption on the graphene surface leads to local changes in material resistance; thus, devices based on graphene may be employed as resistive sensors or in a FET configuration enabling gate voltage tuning. Monolayered graphene and its hybrids with other nanomaterials were proved to detect various gases, including oxidizing and reducing agents [3]–[5]. Nevertheless, fast, stable, and reproducible graphene gas sensors working at room temperature are still in the scope of the current research. The acceleration of surface processes leading to a more pronounced response and faster recovery may be realized by elevated temperature, doping, loading with catalysts, or irradiation in the ultraviolet (UV) spectral range [6]–[8]. UV LEDs of specific wavelengths may provide the energy required for adsorption or desorption of molecules resulting in the shift of the detection limit (DL) towards lower gas concentrations. Simultaneously, highly energetic UV LEDs may degrade the nanostructured material, as reported for carbon nanotubes [9]. Therefore, careful selection of UV wavelength and power are required for reliable sensing. Another option is using pulsed irradiation, which may result in a different material reaction than continuous light. For instance, pulses of various frequencies were reported to influence the MoS_2-based sensors [10]. Although the results of [10] demonstrate that pulsed UV modulation may enhance the sensor response towards gaseous compounds, this approach has not been thoroughly investigated yet.

Herein, we show the graphene-based sensors fabricated in a FET configuration (GFET) for pulsed UV-assisted gas detection. We present DC resistance measurements (sensor resistance between drain and source as a function of gate voltage) collected in the presence of selected gases for irradiated sensor and in the dark. We utilize an inert atmosphere of N_2 and pulsed UV irradiation for graphene surface cleaning. The cleaning procedure allows the preparation of the material surface for more sensitive gas detection by reducing humidity, and pollutant molecules adsorbed to graphene surface. Finally, we discuss and compare our observations on the sensor performance towards ethanol and methane using UV light pulses of selected frequencies.

II. METHODS OF FABRICATION AND MEASUREMENT PROCEDURE

A. *Graphene sensors fabrication*

Fabrication of GFET sensors consists of the following main technological processes. We started with the high-speed electrochemical delamination of commercially available single-layer graphene grown on Cu foil (Graphenea, San Sebastián, Spain). 950PMMA 5.5% was coated on a graphene wafer using spin-coating process prior to transfer to the Si/SiO_2 substrate *via* delamination process with subsequent drying at 130 °C for 24 h. Afterward, PMMA layer was removed by rinsing in acetone. This procedure allowed us graphene deposition on large area substrates up to 1 inch in diameter that is beneficial for gas sensing purposes. After transferring graphene, the layer was patterned by laser lithography and reactive-ion etching (RIE) in oxygen plasma. Finally, the drain and source contacts were formed by Ti(15 nm)/Au(85 nm) thermal evaporation. Silicon substrate with thermally evaporated Cr contacts served as a back gate of GFET. The channel length and width of studied GFETs were $L = 500$ µm and $W = 500$ µm, respectively.

B. *Measurement set-up*

A probe station with titanium needles was used to connect GFET electrodes with the measuring and biasing unit. UV LED of maximum optical power at the wavelength

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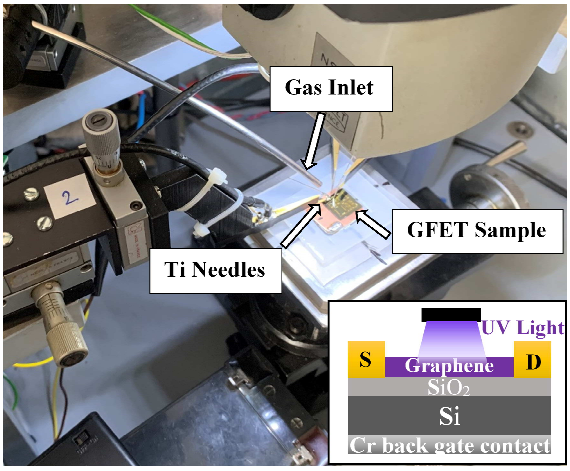

Fig. 1. Photograph of the probe station used for electrical measurements of GFET sensor with a scheme of gas-sensitive structure (inset).

λ = 365 nm (Seoul Optodevice, type T5F) was positioned approximately 0.5 cm from the graphene surface, yielding an optical power density of (0.42 – 0.55) mW/cm^2. The metal pipe connected to the gas distribution system was placed within 0.5 cm from the sample to transport the selected gas to the material. Three calibrating gases were used during the measurements - N_2, 100 ppm of ethanol diluted in N_2, and 200 ppm of methane diluted in N_2. The concentration of selected gases was regulated by mass flow controllers (Analyt-MTC, model GFC17). We kept the overall gas flow at 100 mL/min for each gas, which limited the turbulent flow. All measurements were conducted at room temperature. Fig. 1 presents the photograph of the employed gas detection system and the schematic representation of investigated GFET (Fig. 1 – inset).

C. Electrical measurements

DC resistance measurements were realized using Keithley-4200A-SCS parameter analyzer with two medium power source-measure units (type 4201-SMU). Sensor resistance (R_S) *vs.* gate voltage (U_G) characteristics were collected at selected operating conditions in the U_G range -30 V to +30 V. The drain voltage bias was set to 1 V. Keysight 33500B waveform generator was used for UV pulses modulation. We established square-form pulses of 3.9 V voltage amplitude with a 50% duty cycle at frequencies between 0.1 – 1000 Hz. DC characteristics were collected in the sweeping mode with 2 s-hold time. The sensor response to ambient gases was observed to be much longer than the time of a single UV light pulse, and we observed repeatable sensor responses even at the lowest frequency of 0.1 Hz. During all measurements, the sample was kept inside a metal shielding box to avoid the impact of external electromagnetic interferences.

III. RESULTS AND DISCUSSION

UV irradiation was proved to desorb oxygen species from the graphene surface, leading to the surface cleaning phenomenon [5], [11]. At the same time, weakly bonded oxygen ions may be adsorbed at the surface during irradiation due to a reaction with UV-induced charge carriers (electrons). Graphene acts as a *p*-type semiconductor in air due to oxygen adsorbed on its surface. Thus, adsorption centers are partly occupied. Hence, we employed an inert atmosphere of N_2 and UV irradiation for graphene surface cleaning. A frequency of 1 kHz was adopted for the UV light pulses during the cleaning procedure. The sensor resistance (R_S) rises gradually with irradiation time, as seen in Fig. 2. Additionally, the resistance changes are more pronounced for higher positive gate voltages. After approximately 70 min, R_S starts to stabilize. We may ascribe it to the equilibrium reached at the oxygen-cleaned graphene surface. The overall resistance change during the irradiation process is about 14% at U_G = 30 V. UV irradiation removes previously adsorbed oxygen species, and an inert atmosphere prevents additional oxygen and humidity from adsorption. Modulation of gate voltage towards positive values enhances the differences in sensor resistance under UV irradiation. More noticeable changes at high gate voltages may be attributed to Coulomb interactions between gas molecules and charge carriers (electrons), according to T. Hayasaka *et al.* [12].

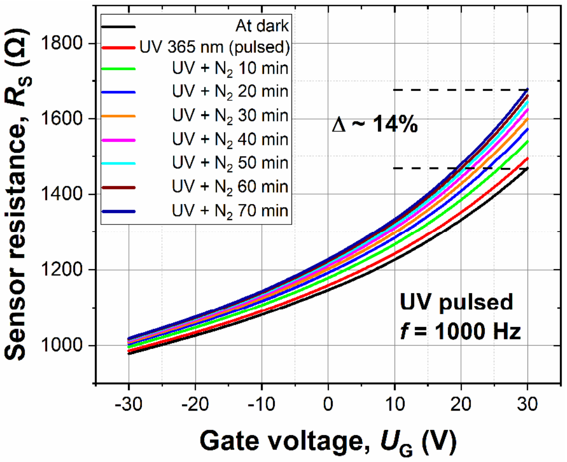

Fig. 2. Sensor resistance R_S as a function of gate voltage U_G during the surface cleaning procedure at UV light (365 nm) pulses frequency of 1 kHz. UV 365 nm (pulsed) characteristic (red line) was collected after 10 min of irradiation in laboratory air.

Fig. 3 depicts GFET-sensor response to 100 ppm of ethanol diluted in N_2 during pulsed UV irradiation. The sample was cleaned according to the procedure mentioned above prior to ethanol detection. It can be observed that the presence of ethanol alters R_S noticeably. Moreover, the higher the frequency of UV light pulses, the greater the R_S. Yet again, the most significant relative change of R_S (5%) can be seen at U_G = 30 V, which is comparable with responses reported previously for this gas of even higher concentrations [13]. Ethanol gas behaves as an electron donor. Since graphene acts as a *p*-type semiconductor in air, increased concentration of minority carriers may lead to R_S growth, as seen in Fig. 3. Analogically, during UV irradiation, the removal of oxygen species leads to re-donating electrons from surface ions, resulting in a similar observation (Fig. 2).

On the contrary, a clear sensor response to methane was not observed. $R_S(U_G)$ characteristics are not influenced by methane gas, regardless of pulse frequency, as seen in Fig. 4. According to other works, methane is very stable in its gaseous form, making it extremely difficult to detect at ambient conditions [14]. Usually, elevated temperatures are required for stable methane sensing. Moreover, only concentrations considerably exceeding 1000 ppm were reported as successfully detected by plain graphene at room

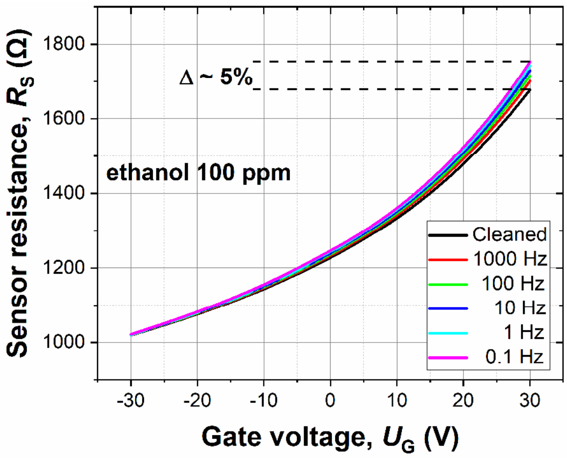

Fig. 3. Sensor resistance R_S as a function of gate voltage U_G in the presence of 100 ppm of ethanol at selected frequencies of pulsed UV irradiation. Characteristics at selected frequency were collected after 10 min of introducing ethanol to the sample (after cleaning procedure).

temperature [15]. Thus, pulsed UV irradiation does not enhance GFET-sensor performance towards 200 ppm of methane.

Fig. 5 compares sensor responses (R_S values) to UV light frequency for ethanol and methane. For ethanol, resistance increases linearly with the decreased frequency, whereas it remains almost unaltered for methane. During UV pulses of lowest frequency (0.1 Hz), the cycles of switching UV light ON and OFF are the longest, leading to more extended interaction of irradiation with the surface and ambient gas during a single pulse in the ON state. We observed different time constants related to the sensor response to ON and OFF states of UV irradiation for ethanol. Thus, the switching frequency of ON and OFF states has an impact on R_S-U_G characteristics. Lower frequencies of UV irradiation allow acceleration of diffusion processes at the graphene surface during the prolonged-ON state, leading to more effective adsorption of molecules of a target gas. Simultaneously, continuous light irradiation could result in concurrent desorption processes. The longer OFF state allows gas molecules to adsorb effectively at earlier UV-generated active centers without being partly desorbed by additional energy carried by UV photons. Subsequent ON state continues to transport and diffuse consecutive portions of gas during continuous gas flow. For continuous or pulsed (high frequencies) light irradiation, the concurrent processes of adsorption and desorption may lead to less pronounced changes in sensor properties. We highlight that the above interpretation is assumptive and believe that it requires further investigation, such as comparison with sensor response for continuous UV irradiation. Nevertheless, the observations on sensing performances of GFET device towards ethanol and methane using pulsed UV irradiation are promising for potential applications.

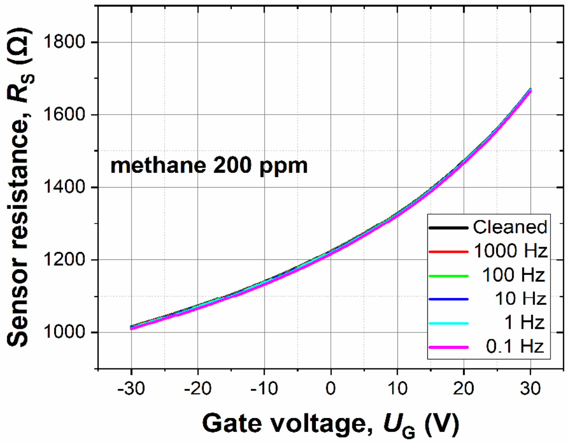

Fig. 4. Sensor resistance R_S as a function of gate voltage U_G in the presence of 200 ppm of methane at selected frequencies of pulsed UV irradiation. Characteristics at selected frequency were collected after 10 min of introducing methane to the sample (after cleaning procedure).

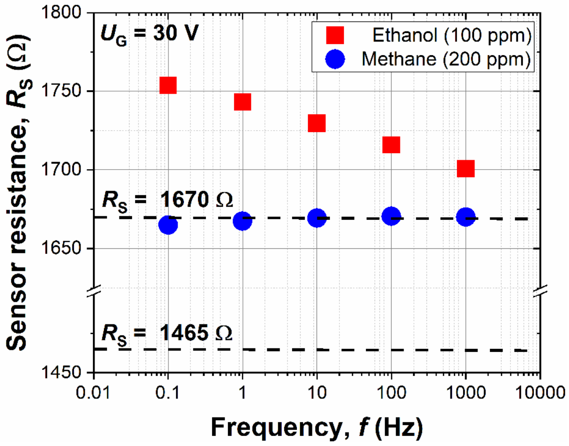

Fig. 5. Sensor resistance R_S at gate voltage U_G = 30 V as a function of UV light pulses frequency. Red squares denote R_S for ethanol (100 ppm), whereas blue circles refer to methane (200 ppm). Horizontal dashed lines refer to sensor resistance in laboratory air, at dark (1465 Ω) and after cleaning procedure in N_2 (1670 Ω).

IV. CONCLUSIONS

We investigated pulsed UV irradiation at selected frequencies for ethanol and methane detection at room temperature. We employed UV-A LED (λ = 365 nm) and an inert atmosphere of N_2 for graphene surface cleaning, allowing uncovering of potential adsorption centers for target gases. UV-cleaned surface with more binding sites enhances the detection process for ethanol (100 ppm). We did not observe any changes in sensor resistance for methane (200 ppm), regardless of light pulses frequency used. For ethanol, the lower the frequency, the higher the sensor response. An increase of graphene resistance agrees with the reducing properties of ethanol when the graphene is a *p*-type semiconductor in ambient conditions. The lower UV pulse frequency provides more time for surface diffusion of gas molecules to active sites in the ON state and more time for effective adsorption in the OFF state. The interpretation mentioned above could explain possible mechanisms of ethanol detection by graphene observed at selected operating frequencies; however, it certainly requires further confirmation. Moreover, future work with UV LEDs of different wavelengths, other gases, and their various concentrations is to be considered. Finally, we show that the UV-modulated graphene-based sensors may be potentially used as room-temperature sensing devices of low-power consumption.

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