Graphene functionalised by laser-ablated V$_2$O$_5$ for a highly sensitive NH$_3$ sensor

Margus Kodu *, Artjom Berholts, Tauno Kahro, Mati Kook, Peeter Ritslaid, Helina Seemen, Tea Avarmaa, Harry Alles and Raivo Jaaniso

Abstract
Graphene has been recognized as a promising gas sensing material. The response of graphene-based sensors can be radically improved by introducing defects in graphene using, for example, metal or metal oxide nanoparticles. We have functionalised CVD grown, single-layer graphene by applying pulsed laser deposition (PLD) of V$_2$O$_5$ which resulted in a thin V$_2$O$_5$ layer on graphene with average thickness of ≈0.6 nm. From Raman spectroscopy, it was concluded that the PLD process also induced defects in graphene. Compared to unmodified graphene, the obtained chemiresistive sensor showed considerable improvement of sensing ammonia at room temperature. In addition, the response time, sensitivity and reversibility were essentially enhanced due to graphene functionalisation by laser deposited V$_2$O$_5$. This can be explained by an increased surface density of gas adsorption sites introduced by high energy atoms in laser ablation plasma and formation of nanophase boundaries between deposited V$_2$O$_5$ and graphene.

Introduction
Graphene, being a thin (semi)conducting material, is a promising gas sensing system. Highly sensitive response, down to single molecule resolution, has been demonstrated with graphene-based devices under laboratory conditions [1-3]. However, in order to develop gas sensing applications working under real conditions, much effort has been dedicated to modification of graphene for improving its gas sensing characteristics. In particular, increasing the selectivity of graphene-based gas sensors is crucial for their future implementation. Recently, the improvement of gas sensing characteristics has been demonstrated with resistive type gas sensors based on single-layer graphene modified by a deposited layer of precious metal [4] or
metal oxide nanoparticles [5]. Also, introduction of suitable defects was shown to have a positive effect on gas adsorption and sensor properties of graphene [6].

Transition metal oxides constitute an important class of catalysts and photosensitizers. Apart from the very first and last 3d elements, scandium and zinc, the rest of the metals possess several oxidation states. The presence of several stable oxidation states serves as a basis of catalytic activity in redox reactions and is most noticeable for vanadium, chromium, and manganese. In particular, vanadium has the highest oxidation state in vanadium pentoxide (V$_2$O$_5$) – a good oxygen transfer catalyst that is (thermally) stable in air and vacuum [7-10]. Therefore, we considered vanadium oxide as a promising material for functionalising a graphene sensor in order to increase its selectivity towards reducing pollutant gases, such as ammonia. Vanadium oxide based films and nanostructured layers have been previously synthesised for gas sensing applications by various methods [11], including pulsed laser deposition (PLD) [12].

PLD is a highly versatile method for relatively well-controlled preparation of thin films, and many advanced composite materials have been produced for diverse applications [13]. The possibility to evaporate practically any solid material, tune the kinetic energy of particles between 0.1 to 1000 eV, as well as the ability to control the amount of deposited material from about 1/100th of a monolayer per laser pulse are the advantages worth mentioning. The method of PLD has recently been applied to improve the nitrogen dioxide (NO$_2$) sensing properties of chemical vapour deposition (CVD) grown, single-layer graphene in our previous work, using ZrO$_2$ and Ag for functionalisation [14].

In the present work, we demonstrate functionalisation of single-layer CVD graphene with a few layers of laser deposited V$_2$O$_5$. The amount and chemical state of vanadium oxide on graphene was characterized by X-ray photoelectron spectroscopy and X-ray fluorescence. The impact of the PLD process on graphene defect structures was investigated using Raman spectroscopy. Based on the electrical conductivity modulation, the room temperature gas sensing properties of the manufactured sensor structure towards ammonia (NH$_3$) and (for comparison) nitrogen dioxide (NO$_2$) gases were investigated.

Results

Figure 1a shows a typical Raman spectrum from graphene placed between the electrodes of the gas sensor structure (see Experimental section). The G and 2D bands peak at $\approx$1590 cm$^{-1}$ and $\approx$2960 cm$^{-1}$, and have full-widths at half-maximum of 11 cm$^{-1}$ and 29 cm$^{-1}$, respectively. These characteristics, together with the ratio of G to 2D band peak intensities of approximately 1:3, correspond to single-layer graphene [15]. The absence of a defect-related D band at $\approx$1350 cm$^{-1}$ indicates extremely low defect density [15,16]. After the PLD of V$_2$O$_5$ onto graphene (for the PLD details, see the Experimental section below), the defect-related D and D’ bands emerge in the Raman spectrum, and at the same time, the G and 2D bands decrease in intensity (Figure 1b).

Figure 2 shows scanning electron microscope (SEM) images of the graphene surface before and after PLD of V$_2$O$_5$. The darker contrasting regions and the lines in the image originate from the Cu growth surface of the CVD process or wrinkles left in the graphene sheet during the transfer process from the copper foil to Si/SiO$_2$ substrate. These features are characteristic for CVD graphene and can also be seen in the SEM image of pristine graphene shown in Figure 2a. The islands of about $\approx$20 nm in diameter from the laser-deposited nanostructured material can be distinguished in the image. It is well known that gas phase species created by laser ablation of solids have a wide distribution of kinetic energy [17]. A considerable fraction of particles can have sufficient energy ($\approx$100 eV) for creation of point defects in the graphene sheet [18]. As a consequence, the Raman lines assignable to point defects or imperfect graphene edges appear. The extent of disorder induced by the PLD process is characterized by the ratio of Raman line intensities $I_D/I_G$. Considering the ratio $I_D/I_G = 2.13$ obtained from Figure 1, and applying the formulae given by Piment et al. [19] and Concado et al. [20], estimates are obtained for the average graphene crystallite size and the distance between point defects of $\approx$7.9 nm and $\approx$7.7 nm, respectively.
The amount of vanadium that was deposited on the sensor substrate was evaluated using X-ray fluorescence (XRF) analysis by measuring the amount of vanadium in the film deposited onto a fused quartz substrate under the identical PLD procedure. According to XRF, the mass thickness of vanadium on the substrate was 0.11 µg/cm². Presuming that all of the vanadium on the substrate belongs to the composition of V₂O₅, and considering the density of crystalline V₂O₅ of 3.38 g/cm³ [21], an estimate for the average thickness of a continuous V₂O₅ layer on graphene is 0.58 nm. In other words, the approximate number of V₂O₅ (001) lattice plane layers is about 2.5.

The oxidation state of vanadium was determined by means of X-ray photoelectron spectroscopy (XPS). Figure 3 depicts the O 1s and V 2p regions in the XPS spectrum measured from the surface of the sample after the PLD process. Because the source was not monochromatic, the V 2p₁/₂ region is not usable for the analysis, owing to the overlap with the Mg Kβ satellite with O 1s peak. The main component of V 2p₃/₂ at a binding energy of 517.4 eV was assigned to V⁵⁺, whereas a faint component at 513.3 eV belongs to V²⁺[V⁵⁺]. The O 1s peak component at 530.9 eV was identified as oxygen bound to vanadium, in agreement with Biesinger’s XPS measurements on vanadium oxide [22]. The main peak component of O 1s at 533.1 eV was attributed to the oxygen in SiO₂ in the silica substrate that can possibly overlap with the C–O component of (partly oxidized) graphene at the same binding energy (533.1 eV) [23]. Thus, according to XPS and XRF analysis, the material deposited on graphene is predominately V₂O₅, with an average thickness of about 0.6 nm. Among other vanadium oxides, V₂O₅ is a relatively stable compound that can be easily deposited by the PLD method [12].

Figure 3: XPS spectra of graphene following PLD treatment with V₂O₅ in the O 1s and V 2p region. A polychromatic Mg Kα source was used for excitation and the satellite peaks were removed.

Figure 4 depicts the time response of a PLD-functionalised graphene sensor to polluting gases NO₂ and NH₃. All the gas measurements in this work were recorded under continuous excitation with ultraviolet (UV) light (λ = 365 nm) at room temperature (RT). Illumination by UV light can enhance the sensing performance of graphene-based gas sensors. An increased gas response and fast recovery under UV irradiation has been demonstrated for pristine and functionalised graphene-based sensors, possibly as a result of cleaning the surface of interfering or passivating gases [24-26]. The effect has been explained by photo-induced desorption of oxygen and water molecules, thus activating additional adsorption sites on graphene for the target gas.
It should be noted that after the PLD of V$_2$O$_5$, the conductivity of the sensor decreases by a factor of 30. According to the Raman spectra (Figure 1), the PLD process is fairly destructive and induces a high concentration of defects to the graphene 2D crystal lattice. These defects decrease the charge carrier mobility in graphene which is reflected in reduced electrical conductivity.

As compared to the pristine sensor, the response to both gases is clearly improved after the functionalisation by PLD. The response to 1 ppm NO$_2$ and 20 ppm NH$_3$ increases from 2 to 12%, and from 6.5 to 26%, respectively. The sensor current shows a clear-cut and reversible response to the test gases NO$_2$ and NH$_3$. As shown in Figure 4, the sign of the conductivity of the graphene sensor changes after introducing another gas (NO$_2$ or NH$_3$) into the test chamber. Graphene is typically a p-type conductor under ambient conditions due to chemical doping by adsorbed oxygen and water molecules [27,28]. Bearing in mind that NH$_3$ acts as a hole acceptor and NO$_2$ as a hole donor [1], the conductivity is expected to increase or decrease, respectively, which is indeed observed. The response to another common reducing gas, the air pollutant carbon monoxide (CO) was also tested. The inset in Figure 4 demonstrates the response of a V$_2$O$_5$ functionalised sensor to 100 ppm CO gas.

In the case of pristine graphene, the response and recovery times of pristine and functionalised sensors for 8 ppm NH$_3$ gas were determined by fitting the time curves with the suitable functions. Either single or double exponential functions were used in the following form:

$$S(t) = \frac{\Delta I}{I_0} = A_0 + A_1 \exp\left(-\frac{t-t_0}{t_1}\right)$$  \hspace{1cm} (1)

$$S(t) = \frac{\Delta I}{I_0} = A_0 + A_1 \exp\left(-\frac{t-t_0}{t_1}\right) + A_2 \exp\left(-\frac{t-t_0}{t_2}\right)$$  \hspace{1cm} (2)

In Equation 1 and Equation 2, $S(t)$ is the relative change of conductance and $t_0$ is the initial time when the respective step-wise change in gas composition was introduced. The characteristic times $t_1$ and $t_2$ are related to the rate constants of adsorption and desorption of gas molecules onto pristine or V$_2$O$_5$-functionalised graphene. In principle, a single exponential type of response (Equation 1) corresponds to the case where there is only one type of adsorption site available for adsorbing molecules at the surface of the graphene sensor. Similarly, the double exponential type of response (Equation 2) may describe the situation where two sites with different adsorption and desorption rate constants are available. The physical aspect of modelling the graphene sensor response is discussed more exhaustively by Jaaniso et al. [29].
and 175 s for the response, and 42 s and 442 s for the recovery. Although the response and recovery kinetics of the functionalised sensor is double-exponential, it is safe to conclude that both the sensor response and recovery times become significantly faster as a result of the laser deposition of V₂O₅ – the response increased by ≈3 times and the recovery by ≈2 times for the functionalised sensor. The amplitude of the response during the 600 s gas exposure increases by 2 times for a gas concentration of 100 ppm, and by 8 times for 8 ppm NH₃. This suggests that the sensitivity is more significantly improved at lower concentrations.

**Discussion**

Perfect graphene is relatively inert because of the lack of dangling bonds and charged atoms on the surface. Consequently, the adsorption energy is due to van der Waals forces, and may be less or comparable to \( k_B T \) (where \( k_B \) is the Boltzmann constant and \( T \) the absolute temperature) for gases at room temperature. The introduction of defects and dopant atoms into graphene can drastically increase both the adsorption of pollutant molecules and the influence of gas adsorption on the electronic properties of graphene [6,30]. For instance, adsorption energy \( (E_a) \) of an NH₃ molecule on regular graphene is relatively small \( (E_a \approx 0.11 \text{ eV} [6,30]) \), but it is much higher for defect (up to 1.5 eV [6,31]) or impurity-doped graphene (up to 1.4 eV [6,30,32]). The introduction of defects and doping atoms into graphene sheets is necessary to enhance the interaction between the target gas molecules and graphene. However, this also results in increased interaction of H₂O and O₂ molecules with graphene [30]. This would result in the situation where active desorption sites are already occupied by strongly bonding O₂ and H₂O and the response to target gas would be slow and small. In some papers, UV light or annealing in vacuum is used to clean the surface of graphene from strongly adsorbed gas molecules, but during adsorption, the excitation is not used [1,26,31]. However, in practical applications there is a constant need to activate the sensor surface by cleaning it of H₂O, O₂ and other adsorbates, which would otherwise passivate it. The illumination by UV light as a tool for initiating or accelerating the desorption was introduced by Chen et al. [33] for carbon nanotube sensors. Thereafter, it was shown that the illumination is beneficial at the adsorption stage as well, acting to considerably enhance the magnitude of the response [34]. The benefits of UV excitation are also clearly observed for single-layer graphene functionalised by a thin layer of laser-deposited ZrO₂ or Ag. First, under UV exposure, the sensor responses were at least 2 to 3 times faster. Second, without UV illumination, the recovery of the signal in pure air was almost absent in the case of ZrO₂, and only partial recovery of the signal occurred in the case of Ag [14].

Generally, graphene-based sensors show much stronger response towards strongly oxidizing, paramagnetic (free radical) NO₂ molecules than to any other gas, including NH₃. The binding energy is large and intermolecular charge transfer can occur when NO₂ adsorbs on either pristine, defective, or doped graphene [6,31]. Table 1 compares the NO₂ and NH₃ responses of our devices, and also of several other sensors reported in the literature, all based on a single-layer graphene. Only qualitative discussion is possible, because in most cases, the gas concentrations differ. It can be seen that most sensors are more responsive to NO₂, as compared to NH₃. However, concerning the relative responses, the results of Yavari et al. [35] are comparable to our V₂O₅-functionalised sensor. According to the measured Raman spectra, the CVD grown graphene used in these experiments contains a relatively large concentration of defects of unspecified nature [35]. The role of graphene defects in the case of NH₃ sensing is well illustrated by Lee et al. [31], where the response to NH₃ gas increased by 600% after creation of defects in the pristine defect-free graphene by reactive ion etching. At the same time, the response to NO₂ gas increased only by 33% [31]. We would like to point out that the graphene sensors functionalised by PLD with Ag and ZrO₂ in our previous work [14] showed a much larger response to

| No. | Material | Response to NO₂ | Response to NH₃ | Ref. |
|-----|----------|-----------------|-----------------|-----|
| 1   | CVD Gr + V₂O₅ | 12% (1 ppm) | 26% (20 ppm) | this work |
| 2   | CVD Gr + ZrO₂ | 110% (1 ppm) | 20% (20 ppm) | this work a |
| 3   | CVD Gr + Ag  | 20% (1 ppm) | 11% (20 ppm) | this work a |
| 4   | exfoliated Gr | 4% (1 ppm) | 4% (1 ppm) | [1] |
| 5   | SiC/Gr + Au  | 55% (0.5 ppm) | 20% (40 ppm) | [4] |
| 6   | defective CVD Gr | 12% (2 ppm) | 40% (40 ppm) | [35] |
| 7   | defective CVD Gr | 55% (200 ppm) | 25% (200 ppm) | [31] |
| 8   | B-doped CVD Gr | 10% (0.02 ppm) | 8% (20 ppm) | [36] |

aSamples are described exhaustively in [14]. The responses to NH₃ are measured in this work.
1 ppm NO₂ than to 20 ppm NH₃ (see Table 1, No. 2 and 3). Thus, decoration of graphene with V₂O₅ lends the sensor some degree of selectivity, and good sensitivity with respect to the reducing pollutant NH₃.

The introduction of dopants and clusters of atoms into graphene strongly increases the interaction with adsorbing molecules, due to an increased charge transfer and formation of chemical bonds between the dopant and adsorbate [6,32]. Moreover, changes in the electronic structure induced by adsorption of molecules are likely to modulate the conductivity of graphene [32].

According to the Raman analysis shown in Figure 1, the PLD process induces a large number of defects in graphene. We propose that during functionalisation of graphene by PLD, the defect creation in the graphene sheet by energetic plasma species is instantly followed by the V₂O₅ cluster growth at the defect site as the PLD process continues. The V₂O₅ clusters are probably chemically bound to the defect sites of the graphene sheet, yielding a strong and stable contact between the two phases. Chemical bonding is accompanied by charge transfer between V₂O₅ clusters and graphene. A similar situation was modelled previously by Lim and Wilcox [37] where large charge transfer and chemical bonding in platinum–graphene systems were observed when Pt nanoclusters were chemically bonded to point defects of graphene sheets. Furthermore, the adsorption of an O₂ molecule onto a platinum nanocluster which was chemically bound to graphene resulted in a large influence on the charge density distribution of the system [37].

V₂O₅ is known for its catalytic properties and as a good NH₃ adsorber [7,8]. The good NH₃ gas sensing properties of V₂O₅ thin films and nanofibers have been demonstrated by Huotari et al. [12] and Modafferi et al. [38]. Two strongly bound adsorption species are typically observed as the result of the reaction of NH₃ with two V₂O₅ adsorption sites, one with a surface OH group, forming positively charged NH₄⁺, and the other with oxygen vacancy, forming species denoted as “coordinated NH₃⁺”. At the same time, the intensity of the V⁵⁺=O related band in the infrared reflectance spectra decreases, which is an indication of the reduction of V₂O₅ [7,9]. The corresponding ammonia oxidation reactions take place on the V₂O₅ catalytic surface. A variety of redox processes are possible, for example:

$$2\text{NH}_3 + 3\text{V}_2\text{O}_5 \rightarrow \text{N}_2 \uparrow + 3\text{H}_2\text{O} \uparrow + 6\text{VO}_2$$

(3)

Ambient oxygen can render the process reversible, as desired for sensor reset, for example:

$$2\text{VO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{V}_2\text{O}_5$$

(4)

Obviously, strongly bound adsorbate species and the accompanying reduction of V₂O₅ can modify the charge distribution in the graphene–V₂O₅ system, thus modulating its conductivity.

According to Gao et al. [10], NO₂ can adsorb to V₂O₅ to form nitrate groups (V⁵+-NO₃), and this process is reversible:

$$\text{V}^{5+} + \text{O} + \text{NO}_2 \rightleftharpoons \text{V}^{5+} \text{-NO}_3$$

(5)

As there are no redox reactions involved in this adsorption process, the influence of NO₂ adsorption on the conductivity of the V₂O₅–graphene system is lower, as expected. Additionally, other energetically favourable adsorption sites can exist at phase boundaries or at the point defects in the parts of graphene exposed to the gas, since the V₂O₅ material is on average only 2.5 layers thick and can cover the graphene surface unevenly.

**Conclusion**

CVD graphene was functionalised by laser deposition of a sub-nanometre layer of catalytically active V₂O₅. The emergence of defect-related D and D’ peaks and the suppression of the 2D peak in the Raman spectrum suggest that a high concentration of defects was introduced during the deposition. According to XPS, the deposited vanadium was in the state V⁵⁺, which is the highest stable oxidation state of this element. As a result, an enhancement in the sensing properties of graphene towards the reducing NH₃ gas was achieved. Such an improvement can arise from the strong adsorption ability of NH₃ on V₂O₅ and possible redox reactions on the surface of V₂O₅, together with the activation of surface processes by using UV light illumination. The changing oxidation state of vanadium can modulate the electrical conductivity of a strongly coupled graphene–V₂O₅ system. Additionally, gas adsorption may be enhanced at the phase boundaries between a very thin nanostructured V₂O₅ layer and graphene substrate.

**Experimental**

Graphene was grown on a commercial 25 µm thick polycrystalline copper foil (99.5%, Alfa Aesar) using a home-built CVD reactor. First, the foil was annealed at 1000 °C in Ar/H₂ flow (both 99.999%, AGA Estonia) for 60 min, and then exposed to the mixture of 10% CH₄ (99.999%, AGA Estonia) in Ar at the same temperature for 120 min. The sample was allowed to cool slowly, 15 °C/min in Ar flow. The as-grown graphene film was transferred onto a Si/SiO₂ substrate by using poly(methyl methacrylate) (PMMA; MW ≈997,000 Da, GPC, Alfa Aesar) as a supporting material. The PMMA solution (1% in chlorobenzene) was spin-coated onto graphene/Cu, dried, and the Cu foil was dissolved in ammonium persulfate solution overnight. The floating PMMA/graphene film was rinsed with deionized water.
and transferred onto the Si/SiO$_2$ substrate (see Figure 6) equipped with Pt electrodes (60 nm thick) that were deposited through a shadow mask by magnetron sputtering. The gap between the electrodes was 1 \times 4 \, \text{mm}$. The sample was dried in air and then heated on a hot plate to allow the PMMA film to soften, which improved the contact between graphene and the substrate. Then the PMMA layer was removed by dissolving in dichloromethane (Alfa Aesar).

The structural characterization of graphene was performed by using a micro-Raman spectroscopic system (Renishaw, inVia) with an excitation wavelength of 514 nm. The vanadium concentration in the deposited layer was analysed with X-ray fluorescence (Rigaku, ZSX 400). The oxidation state of the deposited vanadium was also determined by X-ray fluorescence. The XPS spectra were acquired using a Scienta SES-100 spectrometer. The excitation source was a polychromatic twin-anode X-ray tube (Thermo, XR3E2) with Mg K$_\alpha$ (1253.6 eV) 300 W irradiation at an analyser–source angle of 45°. The semi-quantitative analysis was conducted using the methods described by Seah et al. [39] for quantitative XPS measurements. The spectra were energy calibrated to 284.8 eV (from 284.9 eV) using the C–C peak component of C 1s. The software used for peak fitting was Casa XPS (version 2.3.16).

The measurements of the electrical characteristics and gas sensitivity were carried out with a source meter (Keithley, 2400) in a sample chamber with a volume of 7 cm$^3$ equipped with a gas mixing system based on mass flow controllers (Brooks, model SLA5820). The voltage applied between the electrodes was 100 mV. The gases used in our measurements N$_2$, O$_2$, CO/N$_2$, NO$_2$/N$_2$, and NH$_3$/N$_2$ were all 99.999% pure. A synthetic N$_2$ and O$_2$ air mixture (79% and 21% in the mixture, respectively) was used as a carrier gas and the relative concentration of N$_2$ and O$_2$ gases was held constant during measurements. The gas flow through the sample chamber was kept constant at 200 sccm while the concentration of the test gas was regulated by the ratio of the flow rates of individual gas components. The nominal relative humidity of the testing gas was 20% during the measurements. All the sensor measurements were done at room temperature. The sensor system was exposed to light from a Xe/Hg high pressure lamp (Hamamatsu). The UV wavelength of 356 nm was selected with a narrow-band interference filter (Andover). The light intensity on the sample was 10–20 mW/cm$^2$.

**Acknowledgements**

The research leading to these results was funded by the European Union’s Horizon 2020 Research and Innovation Programme under grant agreement No. 649953, and from the Estonian Research Council by institutional grants IUT34-27 and IUT2-24. The authors would like to thank Indrek Renge for valuable remarks and inspiring discussions.

**References**

1. Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S. Nat. Mater. 2007, 6, 625–655. doi:10.1038/nmat1967
2. Yuan, W.; Shi, G. J. Mater. Chem. A 2013, 1, 10078–10091. doi:10.1039/c3ta11774j
Varghese, S. S.; Lonkar, S.; Singh, K. K.; Swaminathan, S.; Abdala, A. Sens. Actuators, B 2015, 218, 160–183. doi:10.1016/j.snb.2015.04.062
Eriksson, J.; Puglisi, D.; Kang, Y. H.; Yakimova, R.; Lloyd Spetz, A. Phys. B (Amsterdam, Neth.) 2014, 439, 105–108. doi:10.1016/j.physb.2013.11.009
Zhang, J.; Zhao, C.; Hu, A. P.; Fu, Q. Y.; Wang, Z.; Cao, W.; Yang, B.; Placido, F. RSC Adv. 2013, 3, 22185–22190. doi:10.1039/c3ra34380j
Zhang, Y.-H.; Chen, Y.-B.; Zhou, K.-G.; Liu, C.-H.; Zeng, J.; Zhang, H.-L.; Peng, Y. Nanotechnology 2009, 20, 185504. doi:10.1088/0957-4484/20/18/185504
Sun, D.; Liu, Q.; Liu, Z.; Gai, H.; Huang, Z. Appl. Catal., B 2009, 92, 462–467. doi:10.1016/j.apcatb.2009.09.005
Centeno, M. A.; Carriozza, I.; Odriozola, J. A. Appl. Catal., B 2001, 29, 307–314. doi:10.1016/S0926-3373(00)00214-9
Gruber, M.; Hermann, K. J. Chem. Phys. 2013, 139, 244701. doi:10.1063/1.4849556
Gao, X.; Xu, D.; Jiang, Y.; Zhang, Y.; Luo, Z.; Cen, K. J. Mol. Catal. A: Chem. 2010, 317, 46–53. doi:10.1016/j.molcatal.a.2009.10.020
Schneider, K.; Lubecka, M.; Czapla, A. Sensors, Actuators, B 2016, 236, 970–977. doi:10.1016/j.snb.2016.04.059
Huotari, J.; Bjerklund, R.; Lappalainen, J.; Lloyd Spetz, A. Sensors, Actuators, B 2015, 217, 22–29. doi:10.1016/j.snb.2015.02.089
Eason, R. Pulsed Laser Deposition of Thin Films; John Wiley & Sons, New Jersey, 2007. doi:10.1002/0470505212
Kodou, M.; Berhollts, A.; Kahrho, T.; Avaramaa, T.; Kasikov, A.; Nillisk, A.; Alles, H.; Jaaniso, R. Appl. Phys. Lett. 2016, 109, 113108. doi:10.1063/1.4962995
Ferrari, A. C.; Meyer, J. C.; Scardaci, V.; Casiraghi, C.; Lazzeri, M.; Mauri, F.; Piscanec, S.; Jiang, D.; Novoselov, K. S.; Roth, S.; Geim, A. K. Phys. Rev. Lett. 2006, 97, 187401. doi:10.1103/physrevlett.97.187401
Chrisey, D. B.; Hubler, G. K., Eds. Pulsed Laser Deposition of Thin Films; John Wiley & Sons, 1994.
Chisley, D. B.; Hubler, G. K., Eds. Pulsed Laser Deposition of Thin Films; John Wiley & Sons, 1994.
Wang, H.; Wang, Q.; Cheng, Y.; Li, K.; Yao, Y.; Zhang, Q.; Dong, C.; Wang, P.; Schwingschläogl, U.; Yang, W.; Zhang, X. Nano Lett. 2012, 12, 141–144. doi:10.1021/nl2031629
Ferrari, A. C.; Modafferi, V.; Castillo, E.; Gullapalli, H.; Ajayan, P. M.; Koratkar, N. Appl. Phys. Lett. 2010, 100, 203120. doi:10.1063/1.4720074
Yavari, F.; Castillo, E.; Gullapalli, H.; Ajayan, P. M.; Koratkar, N. Appl. Phys. Lett. 2010, 100, 203120. doi:10.1063/1.4720074
Novoselov, K. S.; Terrones, M. Nano Lett. 2010, 10, 3335–3341. doi:10.1021/nl903890f
The definitive version of this article is the electronic one (http://www.beilstein-journals.org/bjnano) terms and conditions: The license is subject to the Creative Commons Attribution License which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. The license is subject to the Beilstein Journal of Nanotechnology terms and conditions: (http://www.beilstein-journals.org/bjnano)