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The effect of an electric field on the graphene hydrogenation rate in inductively coupled plasma

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Results of experimental treatment of monolayer graphene in low pressure inductively coupled hydrogen-containing plasma are described herein. The effect of an electric field on the degree of hydrogenation of samples was studied. Raman scattering spectra of the samples were compared before and after the plasma treatment at various voltages on the sample with respect to a grounded chamber. A method of measuring conductive properties of samples during plasma treatment was proposed. These graphene parameters were measured depending on the plasma treatment time at various voltages on the sample. An assumption is made that the main particles that can react with graphene during plasma treatment are positive hydrogen ions.

Keywords: plasma, graphene, plasma-based chemistry, inductively coupled plasma, graphane.

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Introduction

Since the time when the monolayer graphene was produced [1], the research interest in this material is still very high. Graphene, being a monolayer of hexagonally arranged carbon atoms, has unique properties. For example, the outstanding conductive and thermal properties are among them [2]. On the other hand, zero band gap [3] limits its further application, in particular, in semiconducting devices. One of the methods to control the zero band gap is to perform graphene functionalization with hydrogen atoms, i.e. hydrogenation [4,5]. Moreover, one of the advantages of the functionalization is the maintenance of the unique hexagonal two-dimensional structure when conductive properties are varied [2]. Such hydrogenated graphene can be used to create sensors [6] and transistors [7], and paper[8] also suggests using this substance for advanced high-capacity hydrogen storage.

Plasma-chemical methods are extensively used for the synthesis and modification of various carbon-based substances [9]. Since graphene is inert material, plasma method is one of the promising hydrogenation methods [10,11]. In particular, the main advantage of using the inductively coupled RF-discharge plasma for hydrogenation is in the fact that occurrence of any foreign chemicals, in particular, those preventing electrode erosion, in it is almost avoided. Another advantage is in that the plasma generator parameters may be set or changed during the graphene treatment process. In addition, the plasma method makes it possible to control particles interacting with graphene by applying potential to the sample. For example, this was shown in hydrogen capacitive discharge when high potential with respect to particle energies in plasma was applied to the sample at low treatment time in [12]. Note that the plasma-discharge treatment makes it possible to control the hydrogenation process in more detail compared, for example, with chemical or thermal methods. On the other hand, plasma treatment of materials has disadvantages. For example, even at low power applied to plasma, accelerated particles can induce defect in the sample structure [11]. The objective of the study is to investigate plasma hydrogenation of graphene in „pure“ inductively coupled plasma at various voltages on the sample.

1. Experimental setup

Graphene produced by chemical vapor deposition was used as samples [13]. Spectrum of the initial sample measured using the Raman scattering spectroscopy is shown in Figure 2. Graphene samples exposed on the quartz glass were placed on a metal table into a vacuum chamber. The distance from the sample to the center of plasma-initiating inductor was equal to 30 cm. Preliminary evacuation was performed during 12 h to $p = 10^{-6}$ Torr in order to remove sorbed substances. Then, 140 sccm of argon and 7 sccm of hydrogen were supplied into the chamber using gas flow control valves. These settings were chosen after improvement of the hydrogenation process in the previous study [14]. The chamber pressure during the experiment was kept at $p = 50 \pm 3$ Torr. Plasma discharge was ignited in a quartz tube of 4 cm in diameter with an inductor wound around it. The Advanced Energy Cesar 13.56 MHz generator was used as an RF electromagnetic field source.

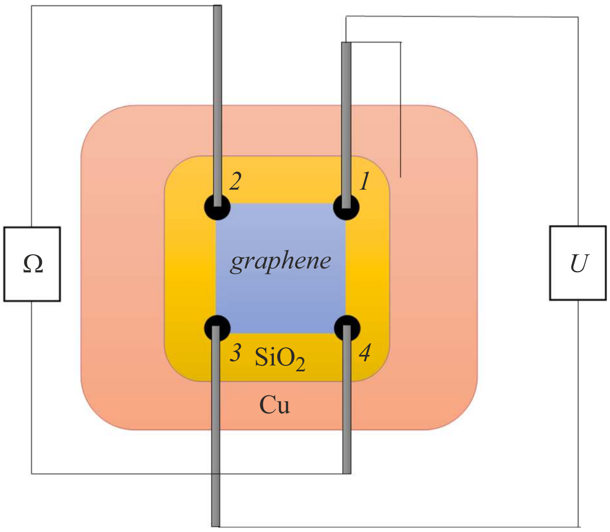

Figure 1. Diagram of contact connection to the sample. *1–4* — indium-gallium paste with pressure contact. Ω — ohmmeter, *U* — voltage source, grounding (in this case, contact *1* is grounded) or other ohmmeter depending on the experiment.

The discharge power was 50 W. The reason for this power was that it was necessary to measure the sample parameters during the experiment and to record these measurements online without additional equipment. Plasma treatment time was 20 min. The plasma setup scheme is similar to that used in the previous study [14].

To measure electric properties of the samples during the experiment, the following circuit was tested (Figure 1). Indium-gallium paste was applied on the corners of the square graphene monolayer with side 7 mm to form contacts to which a metal plate will be pressed later and will not contact graphene. One of the graphene corners on the dielectric quartz glass had electric contact with the metal table to reduce electric field distortions. During plasma treatment, sample resistance was measured diagonally. It is assumed that the amount of hydrogen associated with graphene positively correlates with the sample resistance [10,14]. The resistance of the table, contacts and indium-gallium paste is lower than 1 Ω, and the graphene resistance before plasma treatment is equal to several kΩ hence, it is assumed that graphene parameters are primarily measured. These resistance measurements were performed during plasma treatment. Several experiments were performed. In the first case, the sample and table were not grounded and were exposed to the measured potential of +3.88 V with respect to the grounded chamber. In the second case, the sample and table are grounded. In the third case, a voltage of +2 V with respect to the chamber was applied intentionally to the graphene.

Before and after the plasma treatment, the samples were examined using the Raman scattering spectroscopy. Spectrum peaks according to this technique for graphene are described in [2,10,11,15,16]. Spectra of samples were measured using an the NTEGRA Spectra system (NT-MDT, Zelenograd, Russia) at room temperature. The spectra were measured within 50–3300 cm^{-1} and at a resolution of 2 cm^{-1}. The laser wavelength was 473 nm. The error of spectra recording was 5%.

2. Experimental findings

Figure 2 shows Raman scattering spectra in the monolayer graphene area before (Figure 2 graphene, dashed-dotted line) and after plasma treatment in various conditions. The shown spectra are normalized to peak *G* ($\sim 1580\,\text{cm}^{-1}$). The plasma parameters are described in Section 1. The samples differ in potential with respect to the grounded chamber. The ungrounded sample has a potential of +3.88 V (floating potential) with respect to the chamber. It is assumed that the sample, due to its small dimensions, is quickly charged with respect to the plasma treatment time. The estimated charging time is described in [17]. The second graphene sample was grounded during the plasma treatment. The third sample connection method was in applying a pre-defined voltage of +2 V with respect to the chamber to the sample. All other system settings were identical. Table 1 also shows the peak intensity ratio for these spectra.

According to the measured Raman scattering spectra (Figure 2 and Table 1), it should be noted that the peaks typical for graphene (*G* ($\sim 1580\,\text{cm}^{-1}$) and 2*D* ($\sim 2680\,\text{cm}^{-1}$) [2,18]) remained after the plasma treatment. Note that the typical peak 2*D* has decreased with respect to peak *G* after all experiments. It is suggested that variation of the number of defects affects the peak 2*D*. This corresponds to the statement proposed in [10] that this quantity describes the graphene monolayer in the absence of defects. It is significant that $I(2D)/I(G)$ for the ungrounded sample is higher than in other experimental cases, which suggests that the defect formation rate is affected by the potential on the sample and, in particular, the presence of electric contact between the graphene and

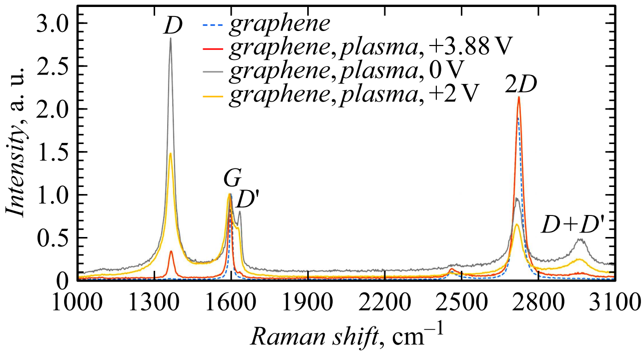

Figure 2. Raman scattering spectra for the graphene samples before plasma treatment (graphene) and after plasma treatment (graphene, plasma) for ungrounded (+3.88 V), grounded (0 V) and (+2 V) samples. Plasma parameters: 140 sccm Ar, 7 sccm H_2, 50 mTorr, 50 W.

Table 1. Peak intensity ratio in the graphene monolayer area before and after plasma treatment for ungrounded (+3.88 V), grounded (0 V) and (+2 V) samples

Intensity, a.u.	Graphene	Graphene, +3.88 V	Graphene, +2 V	Graphene, 0 V
$I(D)/I(G)$	0.02 ± 0.001	0.34 ± 0.02	1.47 ± 0.07	2.8 ± 0.2
$I(D+D')/I(G)$	0.02 ± 0.001	0.09 ± 0.005	0.25 ± 0.01	0.48 ± 0.02
$I(2D)/I(G)$	1.88 ± 0.09	2.1 ± 0.1	0.65 ± 0.03	0.95 ± 0.05

Note. Plasma parameters: 140 sccm Ar, 7 sccm H_2, 50 mTorr, 50 W.

chamber. We suppose that various processes in these plasma conditions, in particular, formation of defects, which, besides lattice failure, also include carbon-hydrogen bonds, are associated with the electric potential value on the sample. On the other hand, the spectra of plasma-treated samples have additional peaks: D ($\sim 1350\,\text{cm}^{-1}$) and $D+D'$ ($\sim 2950\,\text{cm}^{-1}$) [2,16]. According to the increase of peak $D+D'$ due to formation of the carbon-hydrogen bond [16], when the potential on the sample is decreased with respect to the chamber, it is expected that C−H bonds are formed as a defect in these plasma conditions. Note that peak D' ($\sim 1630\,\text{cm}^{-1}$) occurs during hydrogenation due to double resonance in the presence of defects [2,10]. This peak has similar dependence in the potential: the lower the voltage on the sample the higher the intensity. Also note that the defect peak D has the same behavior. $I(D)/I(G)$ in the ungrounded case is higher than that of the hydrogenated graphene on the SiO_2 substrate and is comparable with the free-hanging sample in plasma intercalation from [10]. Also this parameter is comparable with [19], but was obtained during much shorter exposure time. The listed normalized peak intensities for the ungrounded sample are comparable with the data from [12], but were obtained at much lower potential, in another type of discharge and gas composition. Since the degree of hydrogenation that is estimated as $I(D)/I(G)$ increases as the sample potential with respect to the chamber decreases, we suggest that there is interconnection between the C−H bond formation rate and the electric field that accelerates or decelerates the interaction between charged particles and the sample. According to the estimates, the sample may be charged to a potential of 3 V within about 0.1 μs at typical parameters of the experiment. Hence, it is suggested that, within a short time period compared with the total plasma treatment time, such potential is generated on graphene that the sample can further form bonds only with neutral hydrogen that is chemically reactive compared with ionized hydrogen. This is especially noticeable when comparing the degree of hydrogenation of the grounded and ungrounded cases. Positive hydrogen ions are the main particles in this plasma that are necessary for hydrogenation. By changing the potential difference, these particles may more actively reach the sample and form bonds. It is also suggested that during hydrogenation the double C=C bond is broken and replaced with two single bonds: carbon forms the bond with hydrogen ion and a single carbon-carbon bond is formed. Further quite significant reduction of the potential on the sample will not result in the increase in the number of C-H bonds because ions may acquire quite high energy to „knock out“ carbon from the lattice. It is suggested that the balance between the ion energy and additional accelerating potential shall be maintained between the chamber and sample.

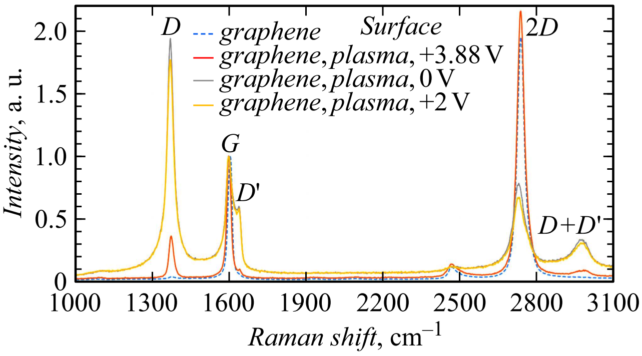

Figure 3. Raman scattering spectra averaged by several points on the surface for the graphene samples before plasma exposure (graphene) and after plasma treatment (graphene, plasma) for ungrounded (+3.88 V), grounded (0 V) and (+2 V) samples. Plasma parameters: 140 sccm Ar, 7 sccm H_2, 50 mTorr, 50 W.

Figure 3 shows the Raman scattering spectra for graphene before and after plasma treatment that were averaged by several points on the sample surface at various voltages on the sample. The confocal microscopy was used to chose several points that belonged to different areas on the sample surface. The selected points has differences in the Raman scattering spectra. It is suggested that these difference are caused by inhomogeneous morphology of the sample surface and bilayer areas. For averaging by several points on the surface within a small peak value range, the difference is 30% on average. Due to this, peak intensities have changed a little compared with the monolayer points. Table 2 shows the peak intensity ratio for the averaged spectra.

According to Figure 3 and Table 2, it is suggested that peak intensity ratio behavior is generally maintained as the potential on the sample varies, but the variation rate itself has changed. In general, hydrogenation is suggested, because an obvious increase of the defect peaks D and $D+D'$ is observed. It is known that $I(D)/I(G)$

Table 2. Peak intensity ratio averaged by several points on the surface for the graphene samples before and after plasma treatment for ungrounded (+3.88 V), grounded (0 V) and (+2 V) samples

Intensity, a.u. surface	graphene	graphene, +3.88 V	graphene, +2 V	graphene, 0 V
$I(D)/I(G)$	0.03 ± 0.01	0.4 ± 0.1	1.8 ± 0.5	2.0 ± 0.6
$I(D+D')/I(G)$	0.03 ± 0.01	0.08 ± 0.02	0.31 ± 0.09	0.33 ± 0.01
$I(2D)/I(G)$	2.0 ± 0.6	2.2 ± 0.7	0.7 ± 0.2	0.8 ± 0.3

Note. Plasma parameters: 140 sccm Ar, 7 sccm H_2, 50 mTorr, 50 W.

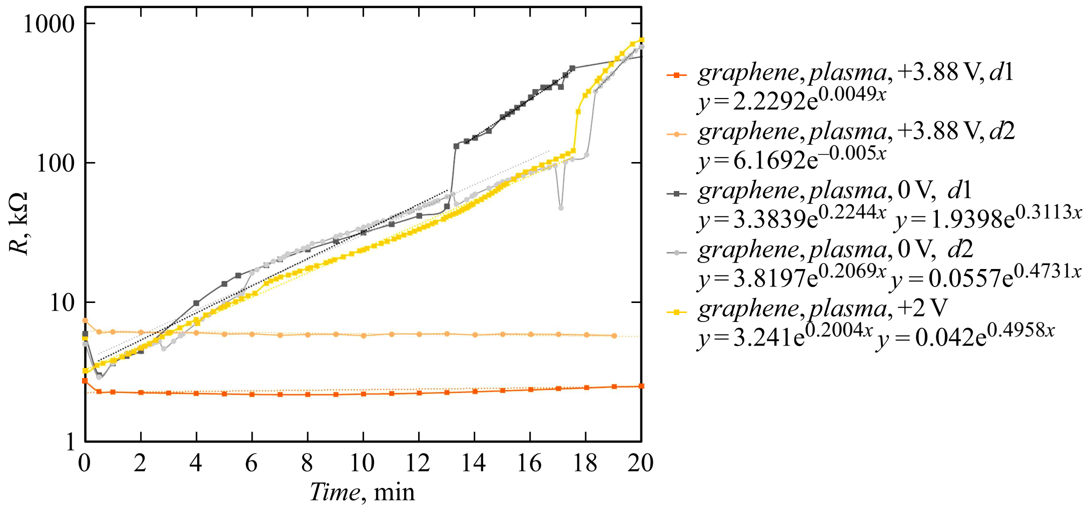

Figure 4. Dependence of resistance of the samples on the plasma treatment time (graphene, plasma) for ungrounded (+3.88 V), grounded (0 V) and (+2 V) samples. Plasma parameters: 140 sccm Ar, 7 sccm H_2, 50 mTorr, 50 W. *d1* and *d2* — two different diagonals. Exponential approximations of these curves are shown near the symbols. In case when there is a resistance jump, then two approximations before and after the jump are shown, respectively.

of the bilayer graphene grows much slower compared with the monolayer graphene as the exposure time increases [18]. In case of the grounded graphene where indicators of the defect peaks D, D' and $D+D'$ with respect to peak G are maximum, decrease of these values is observed considering the whole surface. In two other cases, these indicators vary negligibly or grow. Hence, it is suggested that interaction rates of the monolayer and multilayer part of the sample with hydrogen are different at different potentials, which corresponds to [19].

Figure 4 shows the dependences of the sample resistance during plasma treatment on the time for different voltages on the sample. Resistances for different sample diagonals, except +2 V where one of the diagonal ends is connected to the constant voltage source, are specified and exponential approximations are also provided. In case when there is a resistance jump, then two approximations before and after the jump are shown, respectively. resistance measurement error was 1%. Minor discrepancies in resistance on different diagonals may be associated with sample morphology inhomogeneity.

In the first seconds of plasma treatment, the resistance drops for all samples (Figure 4). This may be associated with gas desorption from the surface due to plasma action. With further treatment, the resistance starts growing in all samples due to formation of defects, in particular, C–H bonds. It is suggested that defects occur mainly in those places near which a defect has already existed in a previous point in time. Since the samples have inhomogeneous morphology, then resistance difference is observed on two diagonals within one order which is ($\Delta R = 5.8\,\Omega - 5.0\,\Omega = 0.8\,\Omega$) for the ungrounded case and ($\Delta R = 7.3\,\Omega - 2.7\,\Omega = 4.6\,\Omega$) for the grounded case.

The ungrounded sample case has the lowest resistance rise rate compared with other cases. Note that the normalized defect peak value in this case (D, $D+D'$, D') is lower. This suggests that the interaction between plasma and graphene takes place quite slowly. This may be explained by quite fast formation of such potential on the sample, and interaction later takes place only with neutral particles or few high-energy ionized particles. Hence, it is suggested that ionized hydrogen is the main particle thanks to which graphene hydrogenation occurs. The sample interacts with other particles no so actively in these discharge ignitions conditions. In two other cases, the resistance growth rate is much higher. Also, at $\sim 100\,\mathrm{k}\Omega$, a jump of the measured quantity occurs and the resistance growth rate increases. Abrupt resistance behavior in the sample may be associated with the graphane growth island combination effect. Supposing that the surface hydrogenation takes place mainly due to expansion of already hydrogenated surface areas, then, with time, current inevitable starts flowing through the hydrogenated areas whose resistance is much higher than that of graphene. Also note that the resistance growth rate before the jump is higher for the ungrounded sample than that of the sample to which $+2\,V$ was applied, that is in turn higher than that of the ungrounded case. This may be correlated with similar behavior of the normalized defect peaks, but it is difficult to chose an explicit dependence.

Conclusion

The paper demonstrates the interaction between the graphene monolayer and hydrogen-containing low pressure inductively coupled plasma. Raman spectra of the samples have been investigated in various operating conditions of the plasma generator. Depending on the method of connection of the graphene samples to the grounded chamber, the intercalation process varies. This may be attributed to the fact that graphene is bonded mainly with positive hydrogen ions. Then the sample potential decrease with respect to plasma increases the number of interactions between graphene and ionized particles. Moreover, a procedure for measuring conductive properties of plasma-exposed graphene has been proposed and tested. It has been measured that the sample resistance grew approximately exponentially with time. It is shown that the resistance variation rate is associated with voltage on the sample with respect to the grounded chamber.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, I.V. Grigorieva, A.A. Firsov. Science, **306** (5696), 666 (2004). DOI: 10.1126/science.1102896

[2] V. Georgakilas, M. Otyepka, A.B. Bourlinos, V. Chandra, N. Kim, K.C. Kemp, P. Hobza, R. Zboril, K.S. Kim. Chem. Rev., **112** (11), 6156 (2012). DOI: 10.1021/cr3000412

[3] P.R. Wallace. Phys. Rev., **71** (9), 622 (1947). DOI: 10.1103/PhysRev.71.622

[4] R. Balog, B. Jørgensen, L. Nilsson, M. Andersen, E. Rienks, M. Bianchi, M. Fanetti, E. Lægsgaard, A. Baraldi, S. Lizzit, Z. Sljivancanin, F. Besenbacher, B. Hammer, T.G. Pedersen, P. Hofmann, L. Hornekær. Nature Mater., **9** (4), 315 (2010). DOI: 10.1038/nmat2710

[5] J.O. Sofo, A.S. Chaudhari, G.D. Barber. Phys. Rev. B, **75** (15), 153401 (2007). DOI: 10.1103/PhysRevB.75.153401

[6] S.M. Tan, Z. Sofer, M. Pumera. Electroanalysis, **25** (3), 703 (2013). DOI: 10.1002/elan.201200634

[7] L. Huang, Z. Zeng. Frontiers Phys., **7** (3), 324 (2012). DOI: 10.1007/s11467-011-0239-3

[8] T. Hussain, A. de Sarkar, R. Ahuja. Appl. Phys. Lett., **101** (10), 103907 (2012). DOI: 10.1063/1.4751249

[9] L.S. Polak, A.A. Ovsyannikov, D.I. Slovetskii, F.B. Vurzel’, *Teoreticheskaya i prikladnaya plazmokhimiya* (Nauka, M., 1975) (in Russian).

[10] D.C. Elias, R.R. Nair, T.M.G. Mohiuddin, S.V. Morozov, P. Blake, M.P. Halsall A.C. Ferrari, D.W. Boukhvalov, M.I. Katsnelson, A.K. Geim, K.S. Novoselov. Science, **323** (5914), 610 (2009). DOI: 10.1126/science.1167130

[11] K.E. Whitener. J. Vacuum Sci. Technol. A, **36** (5), 05G401 (2018). DOI: 10.1116/1.5034433

[12] J.D. Jones, W.D. Hoffmann, A.V. Jesseph, C.J. Morris, G.F. Verbeck, J.M. Perez. Appl. Phys. Lett., **97** (23), 233104 (2010). DOI: 10.1063/1.3524517

[13] M.G. Rybin, A.S. Pozharov, E.D. Obraztsova. Phys. Status Solidi C, **7** (11–12), 2785 (2010). https://doi.org/10.1002/pssc.201000241

[14] A. Vodopyanov, E. Preobrazhensky, A. Nezhdanov, M. Zorina, A. Mashin, R. Yakimova, D. Gogova. Superlattices and Microstructures, **160**, 107066 (2021). DOI: 10.1016/j.spmi.2021.107066

[15] M. Brzhezinskaya, E.A. Belenkov, V.A. Greshnyakov, G.E. Yalovega, I.O. Bashkin. J. Alloys Compounds, **792**, 713 (2019). DOI: 10.1016/j.jallcom.2019.04.107

[16] I. Shtepliuk, I.G. Ivanov, T. Iakimov, R. Yakimova, A. Kakanakova-Georgieva, P. Fiorenza, F. Giannazzo. Mater. Sci. Semicond. Process., **96**, 145 (2019). DOI: 10.1016/j.mssp.2019.02.039

[17] E.I. Preobrazhensky, A.V. Vodopyanov, A.V. Hezhdanov. ZhTF, **93** (7), 884 (2023). (in Russian). DOI: 10.21883/JTF.2023.07.55741.71-23

[18] M. Brzhezinskaya, O. Kononenko, V. Matveev, A. Zotov, I.I. Khodos, V. Levashov, V. Volkov, S.I. Bozhko, S.V. Chekmazov, D. Roshchupkin. ACS Nano, **15** (7), 12358 (2021). DOI: 10.1021/acsnano.1c04286

[19] M. Wojtaszek, N. Tombros, A. Caretta, P.H.M. van Loosdrecht, B.J. van Wees. J. Appl. Phys., **110** (6), 063715 (2011). DOI: 10.1063/1.3638696

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