Hydrogen storage with titanium-functionalized graphene

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Abstract

We report on hydrogen adsorption and desorption on titanium-covered graphene in order to test theoretical proposals to use of graphene functionalized with metal atoms for hydrogen storage. At room temperature titanium islands grow with an average diameter of about 10 nm. Samples were then loaded with hydrogen, and its desorption kinetics was studied by thermal desorption spectroscopy. We observe the desorption of hydrogen in the temperature range between 400 K and 700 K. Our results demonstrate the stability of hydrogen binding at room temperature and show that hydrogen desorbs at moderate temperatures in line with what required for practical hydrogen-storage applications.

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Hydrogen is a very attractive clean fuel since the only combustion waste product is water.\[^1\] Several technical problems hinder its widespread use, among these its storage.\[^1, 2\] In this respect, graphene recently attracted much attention as a storage medium owing to its chemical stability, low weight, and favorable physical-chemical properties for hydrogen adsorption.\[^3\] The storage capacity of graphene can be further increased by surface functionalization.\[^4\] One of the most promising candidates for such functionalization is titanium.\[^5, 6\] Theory predicts gravimetric densities as high as 7.8 wt\% for such systems.\[^5\]

Several reports exist on the behavior of metal atoms and clusters on graphene surface both theoretical\[^7–10\] and experimental.\[^11–17\] Concerning its potential for hydrogen storage, a number of theoretical results are available for various metals on graphene, such as calcium,\[^18–25\] lithium,\[^26, 27\] aluminum,\[^28\] or transition metals\[^4–6, 29, 30\] and transition metal ethylene complexes.\[^31, 32\] A common feature of all these proposals is that the metal atoms (and not the graphene) store the hydrogen. Nevertheless, the role of graphene in this context is fundamental: it acts as a lightweight substrate to carry the metal atoms and contributes thereby to reach high gravimetric densities. However, there are no experimental results published so far which would attempt to verify these proposals. The purpose of this paper is to experimentally investigate hydrogen-storage properties of titanium-covered graphene.

We used monolayer graphene grown on 4H–SiC(0001) as a substrate. It was obtained by annealing 4H–SiC(0001) samples for several minutes in argon atmosphere of 100 mbar at about 2100 K inside a furnace. Graphene quality and the actual number of graphene layers were verified by atomic force microscopy (AFM) and Raman spectroscopy as shown in Fig. 1. Fig. 1(a) shows a 14.4 × 14.4 µm\(^2\) sized AFM phase image of the graphene surface of one of our samples, which shows a strong contrast between mono- and bilayer regions. Fig. 1(b) and (c) show Raman measurements performed on one of our samples. Raman spectra were measured under ambient conditions using an excitation wavelength of 532 nm. The significant Raman peaks for graphene are the G peak and the 2D peak, which changes intensity and position with the number of layers. Although the exact position of the 2D peak depends in addition to the laser wavelength\[^33\] also on the strain in the graphene layer, which originates from the large difference in thermal expansion coefficients between graphene and SiC substrate,\[^34\] a shift of the 2D peak position gives a good indication for the actual number of layers. Fig. 1(b) shows the peak-position map for the Raman 2D
band in one of our samples. Fig. 1(c) shows Raman spectra taken at the two positions indicated in Fig. 1(b). The G and the 2D peak positions are marked in the spectra. The other features originate from the SiC substrate. In our case, the position of the 2D peak is at approximately $2710 \text{ cm}^{-1}$ for monolayer graphene, and at $2740 \text{ cm}^{-1}$ for bilayer graphene. The inset to Fig. 1(c) shows a fit of the bilayer 2D peak with four Lorentzian curves of the same full width at half maximum (FWHM) of $35 \text{ cm}^{-1}$ which confirms the assignment of this area to bilayer graphene. An analysis of the different regions shows that about 85% of the sample is monolayer graphene (blue area in the peak–position map) and 15% is bilayer graphene (red). A similar result was obtained when analyzing Raman FWHM maps of the 2D band.

Hydrogenation experiments and further sample characterization were performed in an UHV chamber with a base pressure of $5 \times 10^{-11} \text{ mbar}$, with a variable-temperature scanning tunneling microscope (STM). The chamber is also equipped with $H_2$ supply, Ti–evaporator, heating stage, and quadrupole mass spectrometer. Details about the microscope are described elsewhere. Before titanium deposition, we annealed the sample at 900 K for several hours to remove adsorbents and to obtain a clean surface. This was done by direct current heating to ensure a homogeneous sample temperature. The high quality of the pristine graphene films is testified by atomically-resolved STM images such as the one in Fig. 2(a) which were routinely obtained and show the hexagonal lattice of graphene. Titanium was deposited on graphene at room temperature using a commercial electron-beam evaporator. The Ti–coverage was calibrated by STM imaging. All temperatures were measured using a thermocouple mounted on the sample holder, directly in contact with the sample and additionally cross–calibrated with a pyrometer. For a better signal–to–noise ratio we used deuterium ($D_2$, mass 4) rather than hydrogen ($H_2$, mass 2). Deuterium is chemically identical to hydrogen; however, we caution the reader that the desorption temperatures might be slightly shifted owing to the well known isotope effect. During thermal desorption spectroscopy (TDS), the mass 4–channel of the mass spectrometer was recorded.

As shown in the STM images in Fig. 2(b) and (c), titanium atoms form small islands on graphene and these islands grow and become more dense at higher coverages. Figure 2(b) shows data taken with a surface coverage of 16%, i.e. 16% of the surface is covered by Ti–islands, while the remaining 84% of the surface is bare graphene. Numerically obtaining
the total volume of the Ti–islands from such images, and assuming a layer distance in
the islands as in hexagonal closed packed bulk Ti \( (d = 0.2342 \text{ nm}) \), this equals 0.56
monolayers (ML) of titanium. Figure 2(c) refers to a sample with a higher Ti–coverage
\( (79\% , 3.3 \text{ ML}) \): the average size of the islands as well as their number is increased. The
histogram in Fig. 2(d) shows the distribution of the island diameters for a surface with
16\% Ti–coverage (cf. Fig. 2(b)). Many islands have a diameter between 5 nm and 9 nm,
while a few reach diameters up to 22 nm, resulting in an average island diameter of around
10 nm for this Ti–coverage. A careful analysis of our STM images shows that for a small
amount of deposited titanium, the percentage of the covered surface is proportional to the
total amount of deposited titanium, while for higher coverage, the islands grow stronger in
height and therefore the surface coverage increases more slowly with respect to the volume
of titanium, until it finally reaches 100\% at around 6.5 ML. The growth of titanium islands
on graphene will be described elsewhere in more detail.

In order to investigate hydrogen storage in the Ti–covered samples, they were exposed
to molecular deuterium \( (D_2) \) for five minutes at a pressure of \( 3.5 \times 10^{-8} \text{ mbar} \) at room
temperature, and then positioned in front of the mass spectrometer. When the pressure was
down to \( 2 \times 10^{-10} \text{ mbar} \) again, we heated the sample at a constant rate of \( 10 \text{ K/s} \) up to a
temperature of approximately \( 850 \text{ K} \). We verified by STM that heating the samples up to
this temperature does not significantly change shape or distribution of the titanium islands.

The resulting temperature–dependent desorption curves of \( D_2 \) are shown in Fig. 3. After
each measurement, a second ramp cycle without deuterium was made to verify that all \( D_2 \)
molecules were actually desorbed during the first cycle. The resulting curves never showed
any signature of \( D_2 \) desorption. In a further control experiment, we exposed pure graphene
without titanium to a deuterium flux and did not see any indication of \( D_2 \) storage (see the 0 \% 
coverage curve in Fig. 3). This is consistent with the well–known fact that although graphene
is capable of binding atomic hydrogen, molecular hydrogen does not stick to a graphene
surface at room temperature. At low titanium coverage, only a small desorption peak
can be detected, but with increasing Ti coverage, peak amplitude increases, and a shoulder
appears at higher temperatures. The position of these features appears to be independent
of titanium coverage. A simple numerical analysis (a fit with two Gaussian curves) leads
to temperatures of around \( (485 \pm 5) \text{ K} \) for the main peak and around \( (560 \pm 10) \text{ K} \) for the
shoulder.
A detailed quantitative analysis of these spectra goes beyond the scope of this letter; however, even from a qualitative standpoint, very useful information can be extracted. First, Ti islands on graphene are indeed capable of storing hydrogen, and the stored amount, which is proportional to the area under the desorption curve, increases with the amount of deposited titanium. Second, the measured desorption temperatures indicate that hydrogen binding is stable at room temperature and that it desorbs at moderate temperatures close to the target temperature for practical applications. Third, the desorption energy barrier can be estimated using the Redhead equation (assuming first order kinetics): \[ E_d/RT = \ln\left(10^{13}/\beta \times T\right) - 3.64 \] with \( \beta = dT/dt \) the heating rate (here 10 K/s), \( E_d \) denotes the desorption energy barrier, \( R \) the gas constant, and \( T \) the measured TDS peak temperatures. This leads to values for \( E_d \) in the range of 1–1.5 eV.

Further insight into the behavior of hydrogen with titanium on graphene can be obtained from a comparison with data available in the literature. Titanium is well known for its catalytic effect in dissociating hydrogen molecules into atoms, similar to what was reported for Pd. These hydrogen atoms can be expected to form bonds either to titanium or to graphene. In the case of binding to graphene, the desorption peak would be expected to decrease when titanium coverage approaches 100%, since there is less and less uncovered graphene surface available. This is not consistent with our data. This suggests that hydrogen is actually binding to titanium. The latter statement is supported by the desorption energy value estimated from our experiments. The binding energy for a dissociated hydrogen molecule on a titanium atom on a \( C_{60} \)-molecule was calculated to be 1.16 eV, which corresponds to approximately 450 K using the Redhead equation. Even though the system is not identical to ours, we expect that binding energies and desorption temperatures be in the same range, as is actually the case. Alternatively hydrogen may also be stored in the titanium islands and forming a titanium hydride complex. The effusion of deuterium from titanium surfaces was studied before by TDS. The desorption spectra of deuterated titanium thin films show a desorption peak around 550 K, again consistently with our data.

In summary, the present measurements demonstrate the suitability of titanium–covered graphene surfaces as a system for hydrogen storage. Clear evidence of stored hydrogen in our samples was reported, based on TDS results. The measured desorption temperatures are high enough for stable hydrogen binding at room temperature and low enough to recover...
the hydrogen at moderate temperatures which render titanium–functionalized graphene a very interesting material system for practical applications in hydrogen storage.

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[1] L. Schlapbach and A. Züttel, Nature 414, 353 (2001).
[2] J. Yang, A. Sudik, C. Wolverton, and D. J. Siegel, Chem. Soc. Rev. 39, 656 (2010).
[3] 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, et al., Science 323, 610 (2009).
[4] K. M. Fair, X. Y. Cui, L. Li, C. C. Shieh, R. K. Zheng, Z. W. Liu, B. Delley, M. J. Ford, S. P. Ringer, and C. Stampfl, Phys. Rev. B 87, 014102 (2013).
[5] E. Durgun, S. Ciraci, and T. Yildirim, Phys. Rev. B 77, 085405 (2008).
[6] A. Bhattacharya, S. Bhattacharya, C. Majumder, and G. P. Das, J. Phys. Chem. C 114, 10297 (2010).
[7] S.-M. Choi and S.-H. Jhi, Appl. Phys. Lett. 94, 153108 (pages 3) (2009).
[8] H. Johll, J. Wu, S. W. Ong, H. C. Kang, and E. S. Tok, Phys. Rev. B 83, 205408 (2011).
[9] X. Liu, C. Z. Wang, M. Hupalo, W.-C. Lu, P. A. Thiel, K. M. Ho, and M. C. Tringides, Phys. Rev. B 84, 235446 (2011).
[10] P. A. Khomyakov, G. Giovannetti, P. C. Rusu, G. Brocks, J. van den Brink, and P. J. Kelly, Phys. Rev. B 79, 195425 (2009).
[11] W. Li, Y. He, L. Wang, G. Ding, Z.-Q. Zhang, R. W. Lortz, P. Sheng, and N. Wang, Phys. Rev. B 84, 045431 (2011).
[12] K. M. McCreary, K. Pi, and R. K. Kawakami, Appl. Phys. Lett. 98, 192101 (pages 3) (2011).
[13] K. Pi, K. M. McCreary, W. Bao, W. Han, Y. F. Chiang, Y. Li, S.-W. Tsai, C. N. Lau, and R. K. Kawakami, Phys. Rev. B 80, 075406 (2009).
[14] S. M. Binz, M. Hupalo, X. Liu, C. Z. Wang, W.-C. Lu, P. A. Thiel, K. M. Ho, E. H. Conrad, and M. C. Tringides, Phys. Rev. Lett. 109, 026103 (2012).
A. Sandin, T. Jayasekera, J. E. Rowe, K. W. Kim, M. Buongiorno Nardelli, and D. B. Dougherty, Phys. Rev. B 85, 125410 (2012).

J. Renard, M. B. Lundeberg, J. A. Folk, and Y. Pennec, Phys. Rev. Lett. 106, 156101 (2011).

C.-L. Song, B. Sun, Y.-L. Wang, Y.-P. Jiang, L. Wang, K. He, X. Chen, P. Zhang, X.-C. Ma, and Q.-K. Xue, Phys. Rev. Lett. 108, 156803 (2012).

X. Yang, R. Q. Zhang, and J. Ni, Phys. Rev. B 79, 075431 (2009).

C. Ataca, E. Aktürk, and S. Ciraci, Phys. Rev. B 79, 041406 (2009).

G. Kim and S.-H. Jhi, J. Phys. Chem. C 113, 20499 (2009).

G. Kim, S.-H. Jhi, S. Lim, and N. Park, Appl. Phys. Lett. 94, 173102 (2009).

H. Lee, J. Ihm, M. L. Cohen, and S. G. Louie, Nano Letters 10, 793 (2010).

P. Reunchan and S.-H. Jhi, Appl. Phys. Lett. 98, 093103 (pages 3) (2011).

E. Beheshti, A. Nojeh, and P. Servati, Carbon 49, 1561 (2011), ISSN 0008-6223.

T. Hussain, B. Pathak, M. Ramzan, T. A. Maark, and R. Ahuja, Appl. Phys. Lett. 100, 183902 (pages 5) (2012).

C. Ataca, E. Aktürk, S. Ciraci, and H. Ustunel, Appl. Phys. Lett. 93, 043123 (pages 3) (2008).

H. An, C.-S. Liu, Z. Zeng, C. Fan, and X. Ju, Appl. Phys. Lett. 98, 173101 (pages 3) (2011).

Z. M. Ao and F. M. Peeters, Phys. Rev. B 81, 205406 (2010).

S. A. Shevlin and Z. X. Guo, Chem. Soc. Rev. 38, 211 (2009).

I. Cabria, M. J. López, S. Fraile, and J. A. Alonso, J. Phys. Chem. C 116, 21179 (2012).

E. Durgun, S. Ciraci, W. Zhou, and T. Yildirim, Phys. Rev. Lett. 97, 226102 (2006).

A. B. Phillips and B. S. Shivaram, Phys. Rev. Lett. 100, 105505 (2008).

A. C. Ferrari, Solid State Commun. 143, 47 (2007).

A. J. Strudwick, G. L. Creeth, N. A. B. Johansson, and C. H. Marrows, Appl. Phys. Lett. 98, 051910 (pages 3) (2011).

D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, and L. Wirtz, Nano Lett. 7, 238 (2007).

S. Goler, C. Coletti, V. Piazza, P. Pingue, F. Colangelo, V. Pellegrini, K. V. Emtsev, S. Forti, U. Starke, F. Beltram, et al., Carbon 51, 249 (2013), ISSN 0008-6223.

G. E. Gdowski and T. E. Felter, J. Vac. Sci. Technol. A 4, 1409 (1986).

T. Zecho, A. Güttler, X. Sha, B. Jackson, and J. Kuppers, J. Chem. Phys. 117, 8486 (2002).

R. M. Wood, Proc. Phys. Soc. 80, 783 (1962).
[40] T. Mashoff, M. Takamura, S. Tanabe, H. Hibino, F. Beltram, and S. Heun, in preparation (2013).

[41] S. Goler, C. Coletti, V. Tozzini, V. Piazza, T. Mashoff, F. Beltram, V. Pellegrini, and S. Heun, J. Phys. Chem. C (????), submitted.

[42] V. Tozzini and V. Pellegrini, Phys. Chem. Chem. Phys. 15, 80 (2013).

[43] D. P. Woodruff and T. A. Delchar, Modern Techniques of Surface Science (Cambridge University Press, 1994).

[44] F. Zuliani, L. Bernasconi, and E. Baerends, J. Nanotechnology 2012, 813872 (2012).

[45] T. Yildirim, J. Íñiguez, and S. Ciraci, Phys. Rev. B 72, 153403 (2005).

[46] T. J. Dhilip Kumar, P. Tarakeshwar, and N. Balakrishnan, J. Chem. Phys. 128, 194714 (2008).

[47] R. Checchetto, L. M. Gratton, A. Miotello, A. Tomasi, and P. Scardi, Phys. Rev. B 58, 4130 (1998).

[48] E. Nowicka and R. Dus, Langmuir 12, 1520 (1996).
FIG. 1: (Color online) a) AFM Phase image (14.4 × 14.4 μm²) of one of our graphene samples, showing the phase contrast between monolayer (ML) and bilayer (BL) regions. b) Peak position map of the Raman 2D peak from one of our graphene samples. Red areas indicate regions where energy position corresponds to bilayer graphene, blue areas correspond to graphene monolayer. Based on such maps, we estimate that a fraction of 85% of our samples is monolayer graphene and the remaining 15% is bilayer graphene. c) Raman spectra measured at the positions indicated in (b), corresponding to monolayer (1) and bilayer (2) regions (offset for clarity). The inset shows a fit of the bilayer 2D peak with 4 Lorentzian curves.
FIG. 2: (Color online) a) Hexagonal graphene lattice (4 × 4 nm$^2$) on the clean surface prior to titanium deposition (V = −0.6 V, I = 290 pA). b) STM image of a 100 × 100 nm$^2$ graphene area with a titanium coverage of 16 % or 0.56 ML (V = 2 V, I = 280 pA). c) 100 × 100 nm$^2$ graphene area with a titanium coverage of 79 % or 3.3 ML. d) Size distribution of the islands at 16 % Ti coverage (corresponding to the surface shown in (b)).
FIG. 3: (Color online) Temperature–dependent desorption spectra of molecular deuterium (m/e = 4) for titanium coverages between 0 % and 100 %. The amount of desorbed deuterium increases with Ti coverage. The desorption starts at around 400 K and reaches a maximum around 485 K. At higher Ti–coverage a shoulder around 560 K emerges.