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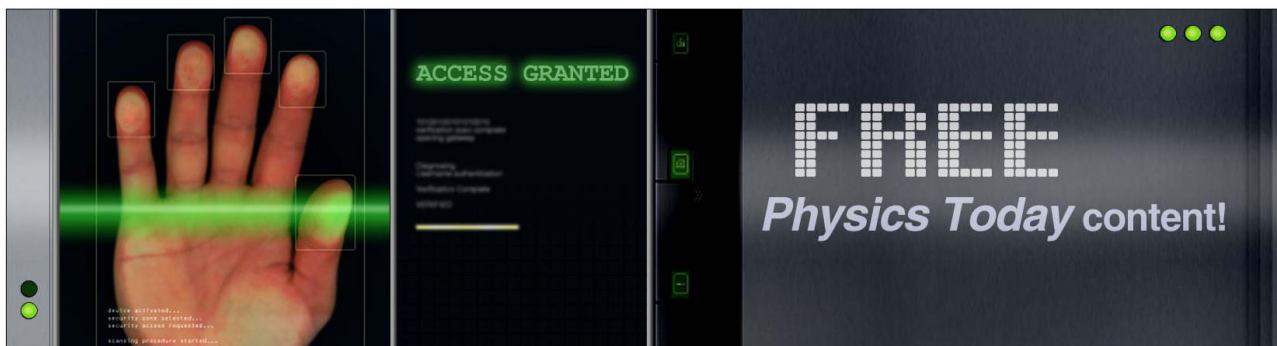
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Room temperature ferromagnetism in partially hydrogenated epitaxial graphene

Lanfei Xie,¹ Xiao Wang,^{1,2} Jiong Lu,³ Zhenhua Ni,⁴ Zhiqiang Luo,⁴ Hongying Mao,³ Rui Wang,¹ Yingying Wang,⁴ Han Huang,¹ Dongchen Qi,¹ Rong Liu,¹ Ting Yu,⁴ Zexiang Shen,⁴ Tom Wu,⁴ Haiyang Peng,⁴ Barbaros Özyilmaz,¹ Kianping Loh,³ Andrew T. S. Wee,¹ Ariando,^{1,2,a)} and Wei Chen^{1,3,a)}

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We report room temperature ferromagnetism in partially hydrogenated epitaxial graphene grown on 4H—SiC(0001). The presence of ferromagnetism was confirmed by superconducting quantum interference devices measurements. Synchrotron-based near-edge x-ray absorption fine structure and high resolution electron energy loss spectroscopy measurements have been used to investigate the hydrogenation mechanism on the epitaxial graphene and the origin of room temperature ferromagnetism. The partial hydrogenation induces the formation of unpaired electrons in graphene, which together with the remnant delocalized π bonding network, can explain the observed ferromagnetism in partially hydrogenated epitaxial graphene. © 2011 American Institute of Physics. [doi:10.1063/1.3589970]

Graphene has been one of the most fascinating materials in the last decade due to its extraordinary quantum electronic properties and great potential for various applications.^{1–3} Much effort has been dedicated to the study of its intrinsic properties, as well as to producing its derivatives by chemical modifications (such as oxidization and hydrogenation) and nanostructuring.^{4–6} It is predicted that zigzag-edged graphene or semihydrogenated graphene sheets would exhibit ferromagnetic properties.^{7–9} In the case of pristine graphene sheets, every carbon atom is sp^2 hybridized with three neighboring atoms and contributes to a delocalized π bonding network. Such configurations lead to its intrinsic nonmagnetic properties. On the other hand, in the case of semihydrogenated graphene, the remnant π bonding network accompanied by the formation of unpaired electrons can induce ferromagnetism.⁹ The realization of such pure carbon (graphene) based ferromagnetic material will be of a great interest for scientific studies and spintronic devices.¹⁰ In this letter we report the observation of room temperature ferromagnetism in partially hydrogenated epitaxial graphene (EG) grown on 4H—SiC(0001).

Various techniques can be used to produce graphene, including micromechanical cleavage or chemical exfoliation from bulk graphite, chemical vapor deposition of hydrocarbons on metal films, and thermal decomposition of single crystal SiC wafers.^{1,11,12} In our experiments, we chose EG grown on commercial single crystal 4H—SiC(0001) wafers for the hydrogenation experiments.¹³ It is able to grow single crystalline and large size (centimeter in our experiment) EG on nonmagnetic SiC with low density of structural defects. This can ensure the reliable characterization by superconducting quantum interference devices (SQUIDs) measurement. Hydrogenation of graphene was realized by radio frequency hydrogen plasma treatment (10 W, 1 Torr) at room

temperature.¹⁴ By controlling the hydrogenation time, EG can easily be partially hydrogenated. Magnetic measurements were performed on partial hydrogenated EG (HEG) by using “Quantum Design” SQUID. Synchrotron-based near-edge x-ray absorption fine structure (NEXAFS) measurements at the SINS beamline in the Singapore Synchrotron Light Source¹⁵ and high resolution electron energy loss spectroscopy (HREELS) were employed to investigate the hydrogenation of EG grown on SiC. For control experiments, SiC reference samples without graphitization were treated with hydrogen plasma at the same time with graphene samples, where no magnetic signal was detected after hydrogenation.

The schematic view of hydrogen attachment on graphene is presented in Fig. 1(a), where different configurations of hydrogen atoms are indicated in different colors (ortho-dimers in yellow, para-dimers in blue and monomers in red). From theoretical calculations,¹⁶ ortho-dimers and para-dimers were predicted to be nonmagnetic; while single hydrogen attachment (monomer) to be magnetic. Raman spectroscopy was performed after hydrogenation and com-

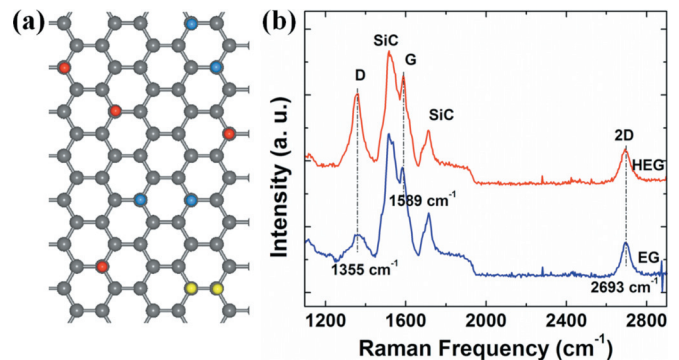


FIG. 1. (Color) (a) Schematic representation of hydrogenated graphene, where different configurations of H atoms are indicated in different colors, i.e., ortho-dimers in yellow, para-dimers in blue, and monomers in red; (b) Raman spectra before and after hydrogenation.

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pared with that of pristine EG in Fig. 1(b).¹⁷ After the hydrogenation, the D peak at 1360 cm^{-1} was enhanced. Such enhancement is most likely due to hydrogen attachment, which breaks the translational symmetry of $\text{C}=\text{C}$ sp^2 bonding.^{5,18}

The magnetic properties of these HEG samples were characterized by SQUID with sensitivity better than 5×10^{-8} emu. The temperature dependence of the magnetization of HEG measured at 10 Oe is shown in Fig. 2(a). As indicated from the curves, a divergence between 1000 Oe field cooling (FC) and zero field cooling (ZFC) clearly emerges starting around room temperature, revealing the magnetic nature of the HEG sample. Figure 2(b) shows magnetization versus applied magnetic field at room temperature for a field range from -500 to 500 Oe. A prominent hysteresis loop is present with the value of saturation magnetization, M_S , approaching $0.2 \mu_B$ per carbon hexagon or benzene ring. Being around 50 times of M_S of the proton irradiated graphite,¹⁹ the magnetism of HEG is remarkably large for a pure carbon-based material. The magnetism measurements of EG, HEG, and hydrogenated SiC (HSiC) without subtracting background are shown in Figs. 2(c)–2(e), respectively. Clearly, only HEG shows ferromagnetic property. To rule out any contamination issue, secondary ion mass spectroscopy (SIMS) studies were performed. After Si or C normalization, the impurity level was found to be less than 1 ppm and within the noise level, indicating the absence of magnetic elements such as Fe, Co, Mn, Ni, or Cr in the samples.²⁰ Furthermore, the magnetic samples do not show any significant deviation in the concentration of magnetic elements compared to the non-magnetic ones (pristine SiC substrate, pristine EG, and HSiC). The ferromagnetism observed in this partial HEG is suggested to come from a disrupted π -bonding induced by hydrogen bonding with carbon atoms accompanied by the formation of unpaired electrons,²¹ while in the case of pure graphene, every carbon atom is sp^2 bonded, resulting in a delocalized π bonding network that leads to its nonmagnetic character as shown in Fig. 2(c).

HREELS is a surface sensitive technique that can be used to probe surface vibrations.²² Energy loss spectra of electrons backscattered from EG and HEG surface at room temperature ($\sim 25^\circ\text{C}$) were acquired separately with an incident angle of 50° , as shown in Fig. 3. Comparing with EG, except the broadening of Fuchs–Kliwer peak,²³ an additional peak arising from $\text{C}-\text{H}$ sp^3 stretching appears at 360 meV after hydrogenation. This peak can be assigned to the vertical $\text{C}-\text{H}$ bonding,²⁴ giving direct evidence for hydrogen attachment on graphene surface. Detailed configurations of hydrogen bonding on EG surface have been studied by STM, where stable monohydrogenated carbon atoms have been observed.²⁵ Theoretical investigations reveal that these monomers could generate localized magnetism.¹⁶ Therefore, a possible origin for the ferromagnetism property observed in HEG sheet could come from the monomer configuration of hydrogen atom attached to graphene as shown by the schematic in Fig. 1(a) highlighted in red.

The covalent attachment of H atom on graphene plane results in the formation of sp^3 hybridized bonding geometry, which can attenuate the delocalized π orbital. In principle, complete hydrogenation of EG will lead to the disappearance of both occupied and unoccupied π orbitals of graphene, and hence results in nonmagnetic property. However, with regard to partial hydrogenation part of the delocalized π network

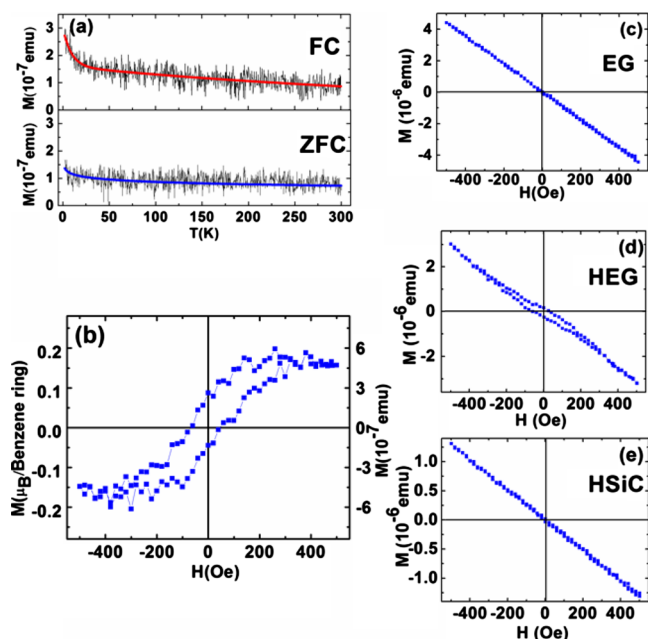


FIG. 2. (Color online) (a) ZFC and FC data showing the temperature variation in magnetization of HEG at 500 Oe; (b) magnetic hysteresis (in unit of Bohr magnetons per benzene ring) of HEG at 300 K after subtracting the antimagnetic background; magnetism signal with background of clean (c) EG, (d) HEG, and (e) HSiC.

would still be preserved, facilitating the long range coupling between those net spin units (unpaired electrons) through the remaining percolated π network.⁹ NEXAFS was performed to evaluate the hydrogenation on EG by comparing the π^* resonance peak intensity before and after hydrogenation.²⁶ Figure 4 shows the carbon K-edge NEXAFS spectra of clean EG and HEG surface at the grazing (G) and normal (N) incident angles (θ) of the linear p -polarized synchrotron light with respect to the surface plane. For pristine graphene in Fig. 4(a), the peak position of π^* band for G and N incidence, with angle of incidence θ at 20° and 90° , respectively, is aligned at $285.3 \pm 0.1\text{ eV}$. The intensity of the π^* absorption at G incidence is much stronger than that at the N incidence, indicating that graphene lies flat on SiC. After hydrogenation, the intensity of the π^* absorption at G incidence is largely suppressed as presented in Fig. 4(b). This reduction is mainly caused by the formation of $\text{C}-\text{H}$ bonding that attenuates the delocalized π network in EG, which is consistent with our HREELS measurement. As indicated in Fig. 4(b), after hydrogenation, a peak at 287.6 eV shows up at

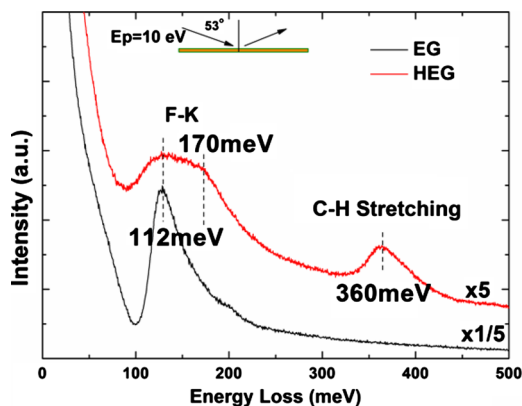


FIG. 3. (Color online) EELS spectra collected in specular direction for EG and HEG.

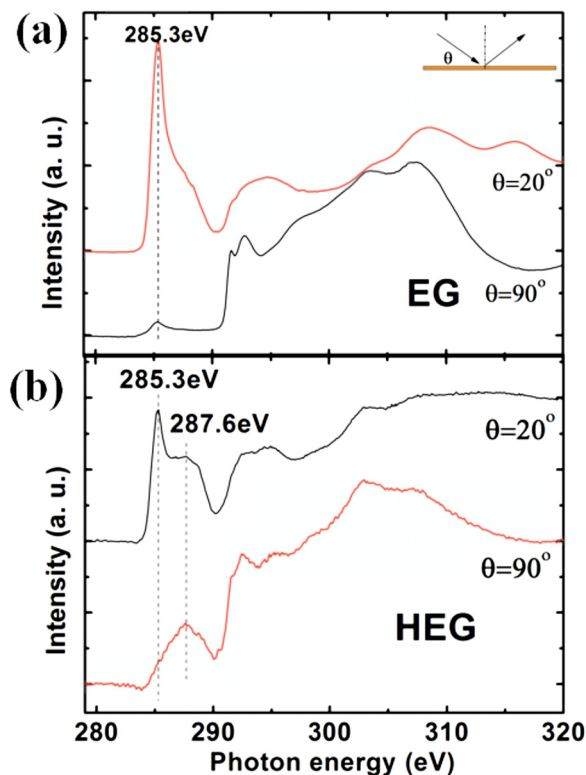


FIG. 4. (Color online) NEXAFS spectra of (a) the clean EG and (b) HEG.

both G and N incidences. In combination with the HREELS results revealing the appearance of the C—H stretching peak, this peak can be assigned to the resonant excitation from C 1s core level to the C—H related unoccupied σ^* band.²⁷ Therefore, partial hydrogenation results in the incomplete decoration of hydrogen monomer on EG. At the same time, the remaining percolated π bonding network after partial hydrogenation allows the existence of a long range coupling among unpaired electrons, facilitating the ferromagnetism in the HEG sample.

In summary, room temperature ferromagnetism was observed in partially hydrogenated EG. Hydrogenation was confirmed by HREELS experiments with the appearance of a C—H stretching peak. The mechanism of the observed ferromagnetism is explained by the formation of unpaired electrons during the hydrogenation process, together with the remnant delocalized π bonding network existing in the partially hydrogenated EG. The fabrication of a variety of spintronic devices requires room temperature ferromagnetic semiconductors. By this controllable hydrogenation method, we can easily turn graphene into a robust room-temperature ferromagnetic semiconductor and open up the possibility of making highly tunable graphene-based spintronic nanodevices.

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