Carbon $p$ Electron Ferromagnetism in Silicon Carbide

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Ferromagnetism can occur in wide-band gap semiconductors as well as in carbon-based materials when specific defects are introduced. It is thus desirable to establish a direct relation between the defects and the resulting ferromagnetism. Here, we contribute to revealing the origin of defect-induced ferromagnetism using SiC as a prototypical example. We show that the long-range ferromagnetic coupling can be attributed to the $p$ electrons of the nearest-neighbor carbon atoms around the V$_{SiVC}$ divacancies. Thus, the ferromagnetism is traced down to its microscopic electronic origin.

Unexpected ferromagnetism has been observed or theoretically predicted for numerous defective carbon based materials and wide-band gap semiconductors such as highly oriented pyrolytic graphite (HOPG), graphene, oxides and SiC$^{1-12}$, which provides an alternative for organic and semiconductor spintronics. As the origin of the ferromagnetism is different from that in conventional $d$-electron ferromagnets, any experimental evidence to reveal its origin will be crucial. Červenka et al.$^{13}$ demonstrated direct evidence that localized electron states at grain boundaries were one of the origins to induce ferromagnetism in HOPG. Oihilation et al.$^{14}$ proved that the ferromagnetism found in graphite originates from carbon $\pi$-states and hydrogen-mediated electronic states. Ugeda et al.$^{15}$ explained the formation of local magnetic moments by single vacancies in graphite. Recently, defect-induced ferromagnetism was found in SiC$^{16-18}$. Divacancies (V$_{SiVC}$) are proven to exist in neutron irradiated and neon implanted SiC$^{19-27}$. Thus a question arises whether it is possible to establish a one-to-one correlation between the local moments and the specific orbitals/electrons in SiC.

On the other hand, SiC has been well known as a kind of economical and practical abrasive and a semiconductor for its application in high-temperature and high-voltage semiconductor electronics. As to our work, the good crystalline quality and the low concentration of impurities (please compare the relevant data in Refs. 8,19,20) can remove the concerns whether the observed ferromagnetism originates from extrinsic factors (e.g. magnetic contamination, see Refs. 21,22). Moreover, the dynamics of defects and their charge states in SiC upon ion irradiation can be obtained by ab initio molecular dynamics simulations$^{23}$, rendering SiC an ideal testbed for the investigation of defects-induced ferromagnetism. Recent studies reveal that SiC could be a material with potential for applications in quantum optics and quantum information$^{24-27}$. Therefore, direct experimental evidence for defect-induced ferromagnetism in SiC will have significant impact on other scientific areas related to defects.

In this paper, 6H-SiC single crystals irradiated with xenon ions are investigated to reveal the origin of its ferromagnetism. We present the results of X-ray absorption near-edge structure (XANES) and X-ray magnetic circular dichroism (XMCD) experiments at both the silicon and carbon K-edges in conjunction with sensitive magnetization measurements and first-principles calculations. These results show that the $p$ electrons of the nearest-neighbor carbon atoms of V$_{SiVC}$ are mainly responsible for the long-range ferromagnetic coupling. Our results provide important evidence for the origin of defect-induced ferromagnetism in SiC.
Results

Magnetization measurements and sample selection. As a prerequisite step, the pristine SiC wafer was checked for trace elements by using particle induced X-ray emission. The amount of transition metal impurities (Fe, Co and Ni) proves to be below the detection limit of around 1 μg/g (result shown in Fig. S1 in the supplementary material). Figure 1(a) exhibits the hysteresis loops of all implanted samples after subtraction of the diamagnetic background. The inset of Fig. 1(a) shows magnetization vs. field for sample 5E12 and the pristine SiC measured at 5 K. The pristine SiC is primarily diamagnetic with a weak paramagnetic contribution (see Figs. S2–S4 in the supplementary material for details). As shown in Fig. 1(a), SiC becomes ferromagnetic upon Xe ion irradiation. The strongest magnetization occurs for the sample 5E12, which is the sample subjected to the lowest fluence and with the least damage to the crystallinity (refer to Fig. S5). With rising fluence, the saturation magnetization ($M_s$) decreases from 0.72 μB/vacancy to around 0.02 μB/vacancy. The decrease of $M_s$ at large defect concentrations has also been observed in proton irradiated graphite. This is very probably due to damage to the crystalline order or due to the unfavorable spin-polarization when the defects are too close to each other. The hysteresis loops measured for the sample 5E12 at 5 K and 300 K after subtracting the magnetic background from the pristine sample are shown in Fig. 1(b), indicating $M_s$ at 300 K is still around half of $M_s$ at 5 K and the transition temperature is higher than 300 K. Therefore, we focus on the sample 5E12 in the following investigation.

Direct evidence for the origin of magnetism. XMCD spectroscopy as an element-specific technique has been used to measure the magnetic contribution from different elements with partially occupied 3d or 4f subshells. Ohldag et al. successfully applied this technique to investigate the magnetism at the carbon K-edge in proton irradiated HOPG. As it is possible to investigate the bonding state in SiC single crystals using XANES spectroscopy, it is also possible to explore the magnetic contribution in defect-induced ferromagnetism in SiC with soft X-ray spectroscopy. Figure 2(a) shows the XANES spectra of the silicon K-edge at 77 K and 300 K, (b) XMCD at the silicon K-edge at 77 K, (c) XANES of the carbon K-edge at 300 K. (d) XMCD at the carbon K-edge at 300 K.

Figure 1 | (a) Ferromagnetic hysteresis loops of samples 5E12, 1E13, 5E13, 1E14 at 5 K after subtracting the magnetic background from the pristine sample. The inset shows the as-measured magnetization vs. field of the sample 5E12 and the pristine sample at 5 K. (b) Hysteresis loops of the sample 5E12 at 5 K and 300 K.

Figure 2 | X-ray absorption spectra measured in EY (electron yield) mode for the sample 5E12 and the pristine sample: (a) XANES of the silicon K-edge at 77 K, (b) XMCD at the silicon K-edge at 77 K, (c) XANES of the carbon K-edge at 300 K. (d) XMCD at the carbon K-edge at 300 K.
the defect-induced ferromagnetism originates from a spin-polarized partial occupancy of the $p_z$ orbitals at carbon atoms close to defect sites in SiC. It is worth noting that an XMCD peak at around 280 eV Fig. 2(d) appears well below the onset of the $p^*$ resonance. This peak was also observed in graphite\textsuperscript{14}. This intriguing feature is not yet fully understood.

**Discussion**

According to the results provided by positron annihilation spectroscopy (see Figure S6 in the supplementary material), divacancies $V_{Si}V_C$ are the dominating defect type in our samples. Note that the nearest-neighbor atoms of $V_{Si}V_C$ include three carbon atoms as well as three silicon atoms. Why is the magnetic signal observed only at the carbon sites? To answer this question, first-principles calculations were employed. As shown in Fig. 3(a), 90% of the spin polarization with a total moment of 2 $\mu_B$ due to one divacancy $V_{Si}V_C$ is contributed by the valence states of the carbon atoms. This explains why XMCD is only observable at the carbon K-edge. Furthermore, when comparing the partial spin-resolved DOS of nearest-neighbor carbon atoms with that of other carbon atoms, it is visible [see Figure 3(b)] that 85% of the magnetic moments originate from the three nearest-neighbor carbon atoms. In the Si-C system, as carbon has higher electronegativity than silicon, unpaired electrons around carbon atoms should be more localized than those around silicon. A Mulliken population analysis indicates that in the unperturbed SiC bulk the Si-C bonds are already polar in accordance with the respective electronegativities: Partial charges of $-0.32$ e on carbon atoms and of $+0.32$ e on silicon atoms are calculated for the pristine bulk at the Mulliken level. In the vicinity of the divacancy carbon atoms show a trend towards larger partial charges ($-0.38$ e), whereas the silicon partial charges close to the divacancy are nearly unchanged. Spin polarization thus mainly appears at those carbon atoms that are located around the divacancies. According to Fig. 3(c), our calculation indicates that most of the magnetic moments (90%) originate from the $p$ states of nearest-neighbor carbon atoms of $V_{Si}V_C$. Due to the attraction of the remaining adjacent silicon atoms, the nearest-neighbor carbon atoms will slightly move away from the $V_{Si}V_C$. This structure change from the unperturbed four-fold bulk coordination to a more planar three-fold bound state is connected with $s$-$p$ rehybridization at the C atoms in the close vicinity of $V_{Si}V_C$. Concomitantly, this distortion will modify the electronic structure locally towards a higher degree of $sp^2$ bonding orbitals and a singly occupied $p$-type lone pair at the C atoms. Thus those outermost orbitals will acquire significant $\pi$ character and the magnetic moments are mainly contributed by $p$ electrons, as shown in Fig. 3(d). This analysis corroborates our interpretation of the XMCD experiment: the XMCD signal of SiC after irradiation is thus assigned to $p$ electrons.

In conclusion, in this work we investigated the magnetic properties of 6H-SiC after xenon irradiation. X-ray absorption spectroscopy at both the silicon and carbon K-edges combined with sensitive magnetization measurements and first-principles calculations are used to understand the origin of defect-induced ferromagnetism. The results give strong evidence that the $p$ electrons of the nearest-neighbor carbon atoms of $V_{Si}V_C$ are mainly responsible for the observed ferromagnetism. These results provide valuable insight into
comprehending the phenomena of defect-induced ferromagnetism in SiC, graphitic and other carbon-based materials, and will encourage the exploration of the origin of defect-induced ferromagnetism in other promising materials such as graphene and oxides.

Methods

Sample preparation. A commercial one-side-polished semi-insulating 6H-SiC (0001) single crystal wafer was cut into pieces for ion irradiation. The concentrations of transition metal impurities (Fe, Co and Ni) prove to be below the detection limit of SRIM \[^{35}\] to be 0.023, 0.047, 0.23, and 0.47, respectively. During implantation, the samples were tilted by 7 degrees to reduce the channelling effect. The corresponding displacements per atom (DPA) values have been calculated by Stopping and Range of Ions in Matter (SRIM) \[^{35}\] to be 0.023, 0.047, 0.23, and 0.47, respectively. During implantation, the samples were tilted by 7 degrees to reduce the channelling effect. The corresponding displacements per atom (DPA) values have been calculated by Stopping and Range of Ions in Matter (SRIM) \[^{35}\] to be 0.023, 0.047, 0.23, and 0.47, respectively.

Measurements. All samples were measured with a superconducting quantum interference device (SQUID-MPMS or SQUID-VSM, Quantum Design). The magnetization is determined according to the total vacancies calculated using SRIM \[^{35}\]. Both XANES and XMCD spectroscopies at the silicon and carbon K-edges were obtained at the Advanced Light Source (Berkeley Lab). The spectra of the silicon K-edge were measured at BL6.3.1 under a magnetic field of –2 and 2 T at 77 K, while the carbon K-edge spectra were measured at BL4.0.2 with the possibility of using a X-ray photon energy as low as 100 eV (note that the carbon K-edge is around 285 eV) and applying an external field of –0.5 and 0.5 T at 300 K. The typical spectral resolution for both beamlines is E/E = ~5000 (see Ref. 14). In the measurements, total electron yield (EY) mode is chosen, which usually collects the signal from the topmost 5–10 nm of the sample \[^{35}\].

Calculation parameters. First-principles calculations were performed using the Cambridge Serial Total Energy Package \[^{35}\]. Spin-polarized electronic structure calculations were performed using the Perdew-Burke-Ernzerhof functional \[^{35}\] for the exchange-correlation potential based on the generalized gradient approximation. The core-valence interaction was described by ultrasoft pseudopotentials \[^{35}\] and to represent the self-consistently treated valence electrons the cutoff energy of the plane-wave basis was set to 310 eV. We calculated the total spin-resolved density of states (DOS) and the partial spin-resolved DOS of silicon atoms and carbon atoms in a 4 × 4 × 1 6H-SiC supercell containing one axial V\(_{\text{Si}}\)-V\(_{\text{C}}\) (\(\Delta V_{\text{Si-C}}\)) \[^{35}\]. The calculation presented in this paper is for neutral V\(_{\text{Si}}\)-V\(_{\text{C}}\). With the minimum distance between adjacent V\(_{\text{Si}}\)-V\(_{\text{C}}\) larger than 12 Å, this structure allows long-range ferromagnetic coupling \[^{35}\]. The content of the spin polarization contribution is determined by comparing the integrated DOS below the Fermi level.

Acknowledgments

The work is financially supported by the Helmholtz-Gemeinschaft Deutscher Forschungszentren (VH-NF-713, VH-VI-442 and VH-PD-146). Y. Wang thanks the China Scholarship Council (File No. 2010675001) for supporting his stay at HDZR. The Advanced Light Source is supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. G. Wang and X. J. Chen also thank the support by the National Natural Science Foundation of China (Grant Nos. 51122211, 9092307, 51072222 and 51272276).

Author contributions

S.Z. conceived the experiment. Y.W. prepared the samples and performed the measurements for magnetic properties. Y.L. and G.W. made the calculation. W.A. carried out the PAS experiment. F.M. did the PIXE measurement. C.J. and E.A. assisted the XAS experiment. O.G., G.S. and D.Z. performed the Raman measurements. S.G., X.C. and M.H. supervised the work. All authors have participated in the manuscript preparation and discussion.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Wang, Y. et al. Carbon p Electron Ferromagnetism in Silicon Carbide. Sci. Rep. 5, 8999; DOI:10.1038/srep08999 (2015).
