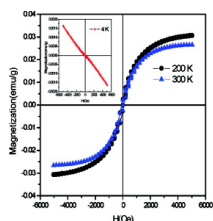## Communication

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Si +C+ Al → Al-doped 4H-SiC

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Observation of Glassy Ferromagnetism in Al-Doped 4H-SiC

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Ferromagnetism (FM) at and above room temperature and spin polarization in the majority carrier band are essential requirements for practical application of diluted magnetic semiconductors (DMSs) in spintronics.[1] However, inconsistencies in literature with respect to the issues such as reproducibility of magnetic properties or dopant segregations make most ones doubt the existence of intrinsic magnetic order and argue for the nature origin in high Curie temperature (T_c) DMSs, obtained by doping transition metal (TM) elements into a semiconductor matrix. Therefore, developing magnetic systems with nonmagnetic elements have been pushed to the frontiers of science since it precludes a spurious FM signal from metal segregation occurring. Recently, the search for macroscopic magnetic order phenomena in various carbon materials has sparked tremendous interest.[2] More recently, the work of Dev and co-workers[3] suggests that it is possible to tune magnetization in wide-gap III nitrides by controlled defects generation and doping. However, experimental observation of FM order in non-TM element-doped wide-gap semiconductors is still lack.

SiC is an important wide-gap semiconductor with more than 200 different polytypes in structures, which are sensitive to the fluctuation of experimental conditions. 4H-SiC has a hexagonal structure ($P6_3mc$) with lattice constants $a = 0.3081$ and $c = 1.0061$ nm and a band gap of 3.26 eV at room temperature. Novel SiC-based DMS devices have been developed and gained considerable attention because of their excellent physical properties.[4] Here, we report the observation of glassy FM in Al-doped 4H-SiC for the first time. The Al element serves two roles: (1) induce long-range magnetic order and (2) stabilize the 4H-SiC polytypes. This study raises some basic questions toward understanding the origin of spin order in wide-gap semiconductor and may open an alternative route toward designing high-T_c SiC-based DMSs.

In a typical run, high-purity silicon (99.999%), carbon (99.9995%), and aluminum (99.997%) powder, supplied by Alfa Aesar, were selected to synthesize the samples (see Supporting Information, SI). Inductively coupled plasma–atomic emission spectrometry (ICP–AES) was used to determine the dopant concentration of aluminum with a ~0.75 atom % in the as-prepared sample. The sample (mass 133.4 mg) was put in a capsule for magnetic measurement (see SI). We characterized the sample structure by high-resolution X-ray diffraction (XRD) and Raman spectroscopy. The cell parameters calculated from the XRD pattern (Figure 1a) are $a = 0.3083(2)$ and $c = 1.0093(6)$ nm corresponding to 4H-SiC (ICDD-PDF: 29-1127, space group $P6_3mc$). Raman spectra (Figure 1b) reveal that the profile of Al-doped 4H-SiC is almost the same as the pristine 4H-SiC wafer, using the folded transverse optic (FTO) mode, which is quite sensitive to the type and degree of crystallization, peaking at 796 cm^{-1}.[5] No contributions from other SiC polytypes or secondary phases within the sensitivity of XRD
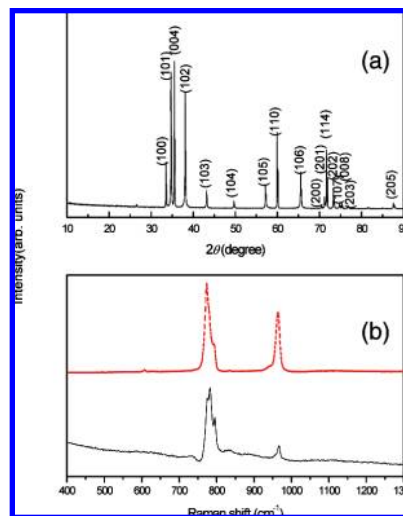

Figure 1. (a) X-ray diffraction pattern of Al-doped 4H-SiC; (b) Raman spectra of Al-doped 4H-SiC (lower curve) and reference 4H-SiC wafer (upper curve).
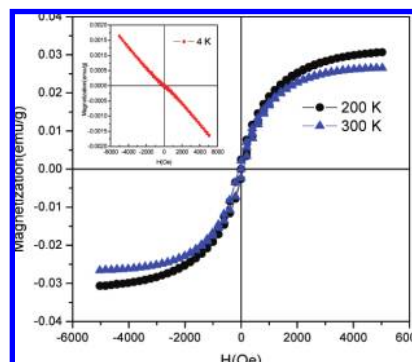

Figure 2. Hysteresis loops for Al-doped 4H-SiC, observed in the range −5 kOe < H < 5 kOe, at 200 K (circles) and 300 K (triangles). Inset shows the hysteresis loops at $T = 4$ K (squares) for undoped 4H-SiC obtained at the same experimental conditions.

and Raman measurement were detected, indicating highly quality single-phase Al-doped 4H-SiC was obtained. Figure 2 shows the variations of magnetization with applied field in the range −5 kOe < H < 5 kOe, at 200 and 300 K, respectively. Distinct hysteresis loops were observed at both 200 and 300 K, indicating FM order dominates the entire temperature range. For the undoped sample, the loop was not observed even at 4 K. Zero-field-cooled (ZFC) and field-cooled (FC) temperature dependence of dc magnetization was measured (see Figure S1). In the field of 1 kOe, the curves exhibit a pronounced FC-ZFC irreversibility as indicated by arrows and a cusp in ZFC curve. A weak irreversibility occurred at ~90 K, and a strong deviation from that in FC run was observed at ~16.4 K in ZFC curve, which is usually ascribed to the freezing of transversal and longitudinal spins, respec-

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tively.[6] This irreversibility between ZFC and FC was suppressed when a higher field of 5 kOe was applied. These features are the fingerprints for spin glass (SG) systems. Moreover, the real part χ' of complex susceptibility is frequency dependent (see Figure S2), exhibiting a peak at $\sim$27 K (T_f). The imaginary part χ'' exhibits a similar sudden onset at T_i, which is also frequency dependent. Here, frequency-dependent ac susceptibility is a convincingly characteristic for a SG behavior. Combining SG with FM order, we conclude that Al-doped 4H-SiC exhibits a glassy FM behavior, which has also been observed in $La_{1-x}Sr_xCoO_3$, $La_{0.7-x}Y_xCa_{0.3}MnO_3$, and $Mn_{3.1}Sn_{0.9}$.[7] Most of glassy behaviors are interpreted in terms of the competition between FM and antiferromagnetic (AFM) interaction, it is also suitable for the as-prepared Al-doped 4H-SiC (see SI). Here, we pay attention to the origin of FM order. To our knowledge, such a robust FM feature has not been observed in non-TM-doping SiC. It should be noted that after the initial discovery, we performed magnetic measurements on a batch of Al-doped 4H-SiC samples. We found that the results of glassy FM were well repeatable except in a few cases in which the bulk sample may be inhomogeneous and do not exhibit FM order at 300 K (see Figure S3). The Al contents were in the range 0.63−0.75 atom %. Trying to obtain sample with higher Al content failed probably owing to Al solubility in SiC.

However, the origin of FM order in such non-TM-doping IV−IV semiconductors is less studied. To investigate the FM origin, we first take account of the purity of the starting materials, which is critical in the determination of the magnetic properties of our bulk sample.[8] Here, the most convincing evidence against the impurity effect is all pristine, as silicon, carbon, and aluminum powder do not exhibit FM signals. Take aluminum for example, the total amount of possible magnetic impurities (Fe, Co, or Ni, etc.) are estimated to be at $\sim$30 ppm. Saturation magnetic moments that arise from these impurities can be calculated to be $\sim$0.004643 emu·g^{-1}, that is, $\sim$7 times less than the magnitude observed in this study. It also excludes the possibility that the FM signal originates from metals clusters formed by magnetic atoms. Further, X-ray emission shows that no contaminants were introduced during the sample preparation. Thus, we conclude that the clear hysteresis loops observed in Al-doped 4H-SiC can be only ascribed to its intrinsic properties. This result inspires a new wave of inquiry into one of the most fundamental and "old" problems: local moment formation and collective magnetization. The most studied DMSs are characterized by the sp−d exchange. FM in true DMSs rely on either carrier-mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect exchange interactions,[9] or percolation of bound magnetic polarons (BMPs),[10] which is suitable for highly resistive specimens. In addition, the d−d double exchange due to hopping between TM d states is another mechanism for FM.[11] Obviously, these models seem not applicable for Al-doped 4H-SiC where no d electrons were involved. As a possible explanation for the formation of local magnetic moment in Al-doped 4H-SiC, we cite ref 2b where unpaired spins arise in a conversion from sp^3 to the mixture of sp^3/sp^2 hybridization. In this study, the partial C−Si bonds (sp^3 configuration with a bond energy of 301 kJ·mol^{-1}) in SiC were converted to C−Al bonds in sp^2 plane configuration when the trivalent aluminum entered into Si sites to induce a mixture of sp^3/sp^2 hybridization. In this process, the unpaired electron is prompted to a higher orbital enabling it to participate in the magnetic ordering. To induce the FM coupling, there should be an effective correlation between these spins moments. We suggest that the extensive structural defects produced by doping aluminum serve as this mediation. No FM feature was observed in the pristine 4H-SiC, prepared under the same conditions (see Figure 2 inset). Here, the combination of produced spin moments and structural defects gives rise to the presence of FM order. However, we cannot absolutely exclude the possibility that magnetic order is

only induced by defects since the itinerant FM could originate substantially from some special structural defects.[12] In fact, the doping Al in SiC may introduce large scales of defects into the lattice, such as vacancies and interstitials. The possible contribution of these defects for FM in Al-doped 4H-SiC needs to be investigated further. In addition, we note that other doping elements (such as Fe, Co, Ni, etc.) can only lead to the mixture of 6H-SiC (main phase) and other SiC polytypes phases under the same conditions. Here, it is speculated that Al element serves as the key role to stablize the SiC crystal structure inherent to 4H and the true mechanism is unclear.

In conclusion, we synthesized Al-doped 4H-SiC, and magnetic properties measurement showed a typical glassy FM feature. We propose a possible explanation for the origin of FM order: the coeffect of sp^2/sp^3 configuration along with the structural defects. Our work demonstrates that the aluminum is a novel dopant in SiC that exhibit two striking features, (1) induces FM order; (2) stabilizes crystal structure, and has exposed the exciting possibility of doping nonmagnetic atoms to control the spin moments in wide-gap semiconductor.

Supporting Information Available: Experimental process, low temperature magnetic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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