Room-temperature ferromagnetism in monolayer WSe$_2$ semiconductor via vanadium dopant

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**Abstract:** Diluted magnetic semiconductors including Mn-doped GaAs are attractive for gate-controlled spintronics but Curie transition at room-temperature with long-range ferromagnetic order is still debatable to date. Here, we report the room-temperature ferromagnetism with a long-range order in semiconducting V-doped WSe$_2$ monolayer synthesized by chemical vapor deposition. Ferromagnetic hysteresis curves are clearly manifested with exclusive Al$_2$O$_3$ passivation via vibrating-sample-magnetometer, exhibiting coercivity remanent to 360K, while retaining high on/off current ratio of ~10$^5$ at 0.1% V-doping. This is also confirmed by the presence of magnetic domains from magnetic force microscopy. V-substituted W atoms keep a V-V separation distance of ~ 5 nm without V-V aggregation, scrutinized by high-resolution transmission-electron-microscopy. Furthermore, the existence of a high saturated magnetic moment without a hysteresis loop at high temperature indicates a transition from ferromagnetism to superparamagnetism. Our findings open new opportunities for using two dimensional transition metal dichalcogenides for future spintronics.

**One Sentence Summary:** We report the room-temperature ferromagnetism with a long range order in semiconducting V doped monolayer WSe$_2$ grown by chemical vapor deposition.
The magnetism of semiconductors can be tuned by modulating carrier concentration with a gate bias. While intrinsic magnetic semiconductors rarely exist in nature (1), incorporation of magnetic dopants into innumerable semiconductors, called diluted magnetic semiconductors (DMSs), allows us to construct an inherent ferromagnetic state with spin-polarized carriers at the Fermi level (2–8). The most typical example is Mn-doped GaAs, which exhibits a gate-controlled magnetic hysteresis, yielding a large number of spintronic devices such as spin-injection sources and memory devices (2, 9–13). Nevertheless, the Curie temperature ($T_c$) of ferromagnetic transition in magnetic semiconductors is scarcely accessible to room-temperature (RT), precluding the use of these materials to practical implementations (2–5, 14). The ferromagnetic state in magnetic metal-doped oxides and nitrides is available at RT but is localized to aggregated metal oxide/nitride nanoparticles without a long-range magnetic order (4).

The ferromagnetic state in van der Waals two-dimensional (2D) materials has been observed recently in the monolayer limit (15–21). Intrinsic CrI$_3$ and CrGeTe$_3$ semiconductors reveal ferromagnetism but the $T_c$ is still low below 60K (20, 21). In contrast, monolayer VSe$_2$ is ferromagnetic metal with $T_c$ above RT but incapable of controlling its carrier density (15). Moreover, the long-range ferromagnetic order in doped diluted chalcogenide semiconductors has not been demonstrated at RT (22–26). The key research target is to realize the long-range order ferromagnetism, $T_c$ over RT, and semiconductor with gate tenability. Here, we unambiguously observe a ferromagnetic hysteresis loop together with magnetic domains above RT in diluted V-doped WSe$_2$, while maintaining the semiconducting characteristic of WSe$_2$ with a high on/off current ratio of five orders of magnitude.

Figure 1A illustrates the schematic for the synthesis of V-doped monolayer WSe$_2$ via chemical vapor deposition (CVD). A metal precursor solution prepared by mixing V and W liquid sources at a given atomic ratio was spin-coated on SiO$_2$ substrate and the substrate was introduced into the CVD chamber with selenium. The metal precursors get decomposed into metal oxides at growth temperature, resulting in monolayer V$_c$W$_{1-x}$Se$_2$, followed by selenization. The atomic ratio of V to W sources in precursor solution can be precisely controlled from 0.1% to 40%, while the hexagonal flakes are retained in a monolayer form (fig. S1). Meanwhile, the dendritic and multilayer flakes are partially generated at higher V concentration. The V atoms are incorporated into monolayer WSe$_2$ with V/W contents similar to nominal values, as confirmed by X-ray photoelectron spectroscopy (fig. S2).

To study the doping effect of vanadium to the electronic properties WSe$_2$, field effect transistors (FETs) of V-doped monolayer WSe$_2$ were fabricated (Fig. 1B). The CVD-grown pristine WSe$_2$ manifests a $p$-type semiconductor with a threshold voltage at $-50$ V. The threshold voltage is shifted to $-10$ V for 0.5% V-doped sample and further increased to $+20$ V for 1% V-doped sample, while retaining high on/off ratio of $\sim 10^5$ and distinct $p$-type behavior. In contrast, the on/off ratio is significantly reduced for $>10\%$ doping samples due to the formation of heavily degenerate V-doped WSe$_2$.

To verify the existence of ferromagnetic order in V-doped WSe$_2$, the ferromagnetic hysteresis was investigated by using a vibrating sample magnetometer (VSM) with the magnetization-magnetic field (M-H) curves of pure and 0.1 % V-doped WSe$_2$ at 3K (Fig. 1C). Although the diamagnetism background caused by the SiO$_2$/Si substrate and tape used for holding the samples appears in both measurements, a big hysteresis loop is revealed at 3K in 0.1% V-doped WSe$_2$, in contrast to no noticeable appearance in pure WSe$_2$. Figure 1D shows the hysteresis loops of the 0.1% V-doped sample at different temperatures after subtracting the diamagnetic background.
The hysteresis loop is clearly manifested above RT, indicating evidence for RT ferromagnetism. The extracted coercivity ($H_c$) and saturated magnetic moment ($M_s$) at various temperatures (Fig. 1E) exhibit ferromagnetism in which $H_c$ decreases as the temperature rises. Meanwhile, $M_s$ rises with temperature, unlike the typical ferromagnetic transition. This behavior is referred to as the ferro-superparamagnetic transition, which is also observed in Mn-doped GaAs (27). The ferromagnetism diminishes, as indicated by the absence of hysteresis loops in the 0.5% V-doped sample at RT but the ferro-superparamagnetic transition with high $M_s$ is still clearly emerging (fig. S3 and S4).

Our measured signals, which are in the range of $\mu$-emu, could be obscured by the artifacts of magnetic impurities (e.g. particles with iron content) during sample preparation and measurement processes (28). Such artifacts can be excluded by several evidences: $T_c$ depends on V concentrations; for example, $T_c$ is ~200K in the 0.5% V-doped sample while it is above 360K in 0.1% V-doped sample. Also, the ferro-superparamagnetic transition of the 0.1% V-doped sample is completely different from the $M$–$T$ characteristics of the ferro-paramagnetic transition of particles with iron content (28).

The long-range ferromagnetic order is confirmed on a microscopic scale by magnetic force microscopy (MFM). Figures 2A–C show the topology, tapping-mode phase, and MFM-mode phase images with a Co-Cr tip of 0.1% V-doped WSe$_2$ at 300K. A 1-nm-thick monolayer is identified in the topology, including some multilayer portions near the flake edge. While the tapping-mode phase image shows no noticeable signal, three distinct features (marked as numbers) are visible in the MFM phase image: (i) large domains separated by domain walls (indicated by white dotted lines), (ii) a dendritic pattern on the flake, uncorrelated with the topology image, and (iii) a strong signal in the multilayer area, correlated with the topology image. Ferromagnetic domain strips of the MFM phase at 150K are clearly manifested (Fig. 2D). The domain strips merge (region a) and split (region b) as temperature increases, strongly implying the domain features originated from magnetic response (Fig. 2E and fig. S5). Several MFM measurements were further performed to ensure magnetism of the V-doped WSe$_2$ (fig S6 and S7). The distinct magnetic phase becomes ambiguous above RT (Fig. 2F) but the magnetic domain walls still retain remanent up to 420K.

To elucidate how the magnetic domains are modulated with doping concentration, we further conducted MFM for 0.5% and 2% V-doped WSe$_2$ (Fig. 2G and fig. S8). A strong contrast phase within the flake still emerges from the 0.5% sample up to 270K and dendritic patterns appear at high temperature. The dendritic patterns in MFM mapping are clearly revealed at above 300K in both 0.5% and 2% V-doped samples, which is reminiscent in PL and Raman mapping (fig. S9 and S10). Intriguingly, the magnetic transition relies on V contents, i.e., $T_c$ at ~270K in 0.5% and ~180K in 2% V-doped sample, which is fairly correlated with the VSM data. The MFM measurements with the tip magnetized vertically and horizontally were carried out. The amplitude of the magnetic signals is much stronger with vertical magnetized tip than with horizontal one (Figs. 2H and 2I). Additionally, the sign of the phase (compared to the SiO$_2$ background) is converted in some domains. For example, the contrast of region (b) is positive with vertical magnetized tip, whereas it is negative with horizontal one. This indicates the magnetic force changes from repulsive to attractive force, which is also solid evidence for the magnetic response. We note that the ferromagnetic properties of V-doped WSe$_2$ are very sensitive under ambient conditions. The V-doped WSe$_2$ samples passivated by Al$_2$O$_3$ or Se allow us to preserve inherent ferromagnetic properties. No hysteresis loop was eminent in the samples.
without passivation (fig. S11). It is further confirmed by MFM measurements (figs. S12 and S13).

For investigating the proximity of V atoms with V composition, we provide annular dark field scanning transmission electron microscopy (ADF-STEM) images for 0.1% and 2% V-doped WSe$_2$ (Fig. 3). A well-crystallized 2H–WSe$_2$ structure is clearly demonstrated with W (bright) and Se (grey) sites with additional V (dark) atoms, as is consistent with the intensity profile with simulated images (Fig. 3A–D). Well-distributed V atoms in both samples without any clustering indicates that the magnetic properties of V-doped WSe$_2$ did not originate from phase segregation of vanadium but rather result from interaction between V atoms via host WSe$_2$.

To investigate the correlation between $T_c$ and V composition, we analyzed the concentration for RT-ferromagnetic 0.1% and low-temperature ferromagnetic 2% V-doped samples (Figs. 3E and 3F). Three impurities are clearly identified after Wiener-filter false coloring (fig. S14): Se-vacancy in WSe$_2$ (WSe), V-substitution into W site in WSe (VSe), and VSe$_2$. Five STEM images of each sample were thoughtfully analyzed for reliable statistics (fig. S15). The real V concentration of nominal 0.1% and 2% V-doped samples are similar to 0.1 ± 0.01% and 1.0 ± 0.07 %, respectively (fig. S16).

Chalcogen defects can influence magnetic properties of TMDs (29). However, Se-vacancy concentration is irrespective of the V composition (approximate 1% or 10$^{13}$ cm$^{-2}$ in both 0.1% and 2% samples). This strongly implies that the RT-ferromagnetism is not attributed by Se-vacancies. The role of V-substituted forms (VSe or VSe$_2$) is as yet unclear for the magnetism of V-doped WSe$_2$. However, the ratios of VSe to total V atoms (VSe+$\text{VSe}_2$) are similar in both 0.1% and 2% V-doped samples (fig. S17), indicating that VSe or VSe$_2$ doping concentration is closely correlated to each other for discernible $T_c$.

We next explore the first and second nearest neighbor distances between V atoms (Fig. 3H). The average V-V neighbor distance is much longer in 0.1% (50 Å, or ~15 unit cells) than in 2% (18 Å, or ~5 unit cells) V-doped samples. The long-range ferromagnetic order in such a long neighbor distance in 0.1% V-doped sample is highly probable by the Zener mechanism, playing an important role with free carriers (14).

In summary, we have successfully synthesized V-doped WSe$_2$ in monolayer, which reveals RT dilute ferromagnetic semiconductors. The existence of the ferromagnetic ordering is confirmed both on macroscopic scale by VSM and on microscopic scale by MFM. Our work opens a direct route to demonstrate practical applications of TMDs in spintronic devices at RT.

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**Supplementary Materials:**

Materials and Methods

Supplementary Text

Figures S1-S18

References (30-31)
Fig. 1. Synthesis of semiconducting V-doped monolayer WSe$_2$ and ferromagnetic characteristics. (A) Schematic of synthesis of V-doped WSe$_2$ by mixing liquid W with V precursors. (B) Source-drain current (biased at 1V) with the gate bias for V-doped WSe$_2$ field-effect transistors with various V-doping concentrations. (C) In-plane $M$–$H$ curves of pristine and 0.1% V-doped WSe$_2$ on SiO$_2$/Si substrate passivated by Al$_2$O$_3$ at 3K. Diamagnetism signal originates from the SiO$_2$/Si substrate and tape used for holding the samples. A clear hysteresis loop appears in V-doped sample. (D) Temperature-dependent $M$–$H$ hysteresis loops, (E) coercive field ($H_c$), and saturated magnetic moment ($M_s$) in 0.1% V-doped WSe$_2$ after subtraction of diamagnetism background.
Fig. 2. MFM with magnetic domains in 0.1% and 0.5% V-doped WSe$_2$. (A) Topology, (B) tapping-mode phase, and (C) MFM phase images of 0.1% V-doped WSe$_2$ at RT. (D) MFM phase image of 0.1% V-doped WSe$_2$ taken at 150K. (E) Temperature-dependent transition of magnetic domains and (F) related phase profiles in the white-dotted box in (D). (G) Temperature-dependent MFM phase images of 0.5% V-doped WSe$_2$. (H) MFM response of 0.5% V-doped WSe$_2$ with different magnetized directions at 240K. (I) Average phase signal of regions indicated by the letters in (H). The phase value for SiO$_2$ is set to zero for the reference.
Fig. 3. Atomic structure of V-substituted WSe$_2$ observed by STEM. (A) ADF-STEM images of V-doped monolayer WSe$_2$. (B) Experimental, (C) simulated images, and (D) their intensity profiles for V-doped WSe$_2$. False-color Wiener-filtered STEM images of (F) 2% V and (E) 0.1% V-doped WSe$_2$. Statistical analysis of V-doped WSe$_2$ for (G) V substitution, Se vacancies, VSe species, and (H) vanadium nearest neighbor distances.