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ABSTRACT

Magnetism in two-dimensional van der Waals materials has received significant attention recently. The Curie temperature reported for these materials, however, has so far remained relatively low. Here, we measure magneto-optical Kerr effects under a perpendicular magnetic field for van der Waals ferromagnet $Cr_2Ge_2Te_6$ and its heterostructures with antiferromagnetic insulator NiO. We observe a notable increase in both Curie temperature and magnetic perpendicular anisotropy in $Cr_2Ge_2Te_6$/NiO heterostructures compared to those in $Cr_2Ge_2Te_6$. Measurements on the same exfoliated $Cr_2Ge_2Te_6$ flake (on a SiO_2/Si substrate) before and after depositing NiO show that the hysteresis loop can change into a square shape with a larger coercive field for $Cr_2Ge_2Te_6$/NiO. The maximum Curie temperature (T_C) observed for $Cr_2Ge_2Te_6$/NiO reaches ∼120 K, which is nearly twice the maximum $T_C \sim 60$ K reported for $Cr_2Ge_2Te_6$ alone. Both enhanced perpendicular anisotropy and increased Curie temperature are observed for $Cr_2Ge_2Te_6$ flakes with a variety of thicknesses ranging from ∼5 nm to ∼200 nm. The results indicate that magnetic properties of two-dimensional van der Waals magnets can be engineered and controlled by using the heterostructure interface with other materials.

Recently, magnetism in layered van der Waals (vdW) materials has attracted great attention because of their unique magnetic properties stemming from their two-dimensional (2D) nature.[1,2] Such layered vdW materials provide an opportunity to fabricate heterostructures free from constraints in conventional film growth and promise a unique route to explore new functionality of these materials based on the electric field and crystalline symmetry.[3,4] One of the major issues in vdW ferromagnets is that the ferromagnetic transition temperature (Curie temperature) is relatively low. CrI_3 and $Cr_2Ge_2Te_6$ were reported as atomically thin-form ferromagnets in 2017, where the Curie temperature ranges from 30 K (bilayer $Cr_2Ge_2Te_6$) to 45 K (monolayer CrI_3), being intriguingly low compared to the bulk values of 61 K (bulk CrI_3) and 66 K (bulk $Cr_2Ge_2Te_6$).[1,2] To enhance the Curie temperature, a variety of approaches using interface and gap engineering have been proposed including the dielectric effect, spin–orbit coupling proximity, charge transfer, and interface hybridization.[5] However, only a few approaches have been implemented and reported so far, such as electric gating.[4,6] Therefore, it is important to search for other effective approaches to enhance the Curie temperature. Here, we study magnetic properties in heterostructures between antiferromagnet NiO and vdW ferromagnet $Cr_2Ge_2Te_6$. We will report magneto-optical Kerr effects (MOKEs) and detect hysteresis arising from ferromagnetism.

$Cr_2Ge_2Te_6$ was earlier reported by Carteaux *et al.*,[7] and recently, there is significantly increasing interest because this is a layered two-dimensional magnet with mechanical cleavability down to atomically thin layers. The $Cr_2Ge_2Te_6$ single crystals used in this work were grown via a self-flux technique. First, 100 mg of Cr powder, 200 mg of Ge powder, and 2 g of Te were sealed in a quartz tube. The mixture

was heated to 1050 °C and held for 30 h, and then, it was cooled down to 475 °C in 10 days, and finally, the Ge-Te flux was removed using a centrifuge at this temperature. The magnetic properties of the bulk crystals were characterized by magnetometry using the MPMS (magnetic property measurement system), and the Curie temperature was found to be $T_C \approx 66$ K from the minimum of dM/dT curves (measured with the magnetic field of 50 mT in the c-axis). The observed magnetic properties were consistent with the previous reports.[1,4,7–13] $Cr_2Ge_2Te_6$ crystals were mechanically cleaved onto a silicon substrate in ambient conditions (with the SiO_2 thickness of 285 nm). The thickness of the flakes was characterized by using an atomic force microscope. Atomically thin flakes were visible with thickness-dependent color contrast due to the interference effect as shown in Fig. 1(a). Sputtering was performed using a NiO target with a base pressure of ca. 1×10^{-5} Pa, an Ar pressure of 0.2 Pa, and 200 Watt RF power. Various deposited NiO films with different thicknesses ranging from 20 nm to 100 nm are explored in this work. After the sputtering of the NiO layer, the color of both the silicon substrate (with NiO) and the

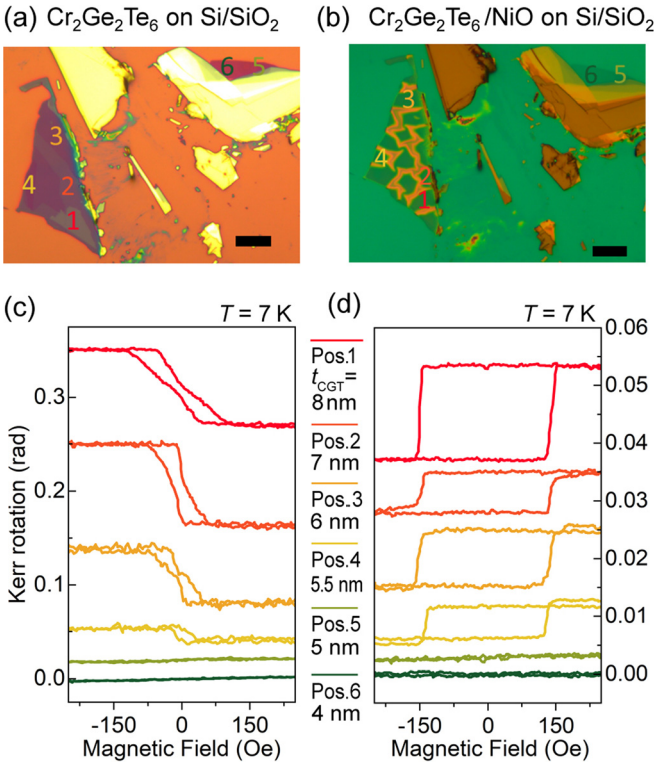

FIG. 1. (a) and (b) Optical microscopy image of $Cr_2Ge_2Te_6$ (CGT) flakes on a Si/SiO_2 substrate, before (a) and after (b) the deposition of NiO. After the deposition of NiO with a thickness of 20 nm, the optical contrast changes because the interference condition is modified. The scale bar is 10 μm. (c) Measured magneto-optical Kerr effect (MOKE) curves at the temperature of 7 K, with the magnetic field perpendicular to the substrate. The curves from different positions (labeled 1–6) are shifted vertically. The positions are marked in the images (a) and (b). The CGT-flake thickness at each position was measured by atomic force microscopy. (d) MOKE curves measured at the same positions after NiO deposition. Perpendicular anisotropy is strongly enhanced, and square shaped hysteresis curves are observed. The opposite sign of the MOKE hysteresis curves between (c) and (d) is supposedly due to the different optical constants of the sample without (c) and with (d) the NiO overlayer.[14]

$Cr_2Ge_2Te_6$ flakes changed as shown in Fig. 1(b) because the interference condition was modified.

Polar magneto-optical Kerr Effect (MOKE) measurements were performed in an Oxford MicrostatMO system in the Faraday configuration. A temperature stabilized laser diode (635 nm in wavelength) was used to deliver a linearly polarized laser beam that was focused onto the sample at normal incidence using a 0.6 NA 100X long working distance objective. The estimated power delivered to the sample is less than 3 μW. The laser beam was intensity modulated using a chopper, and the reflected beam was sent through a Wollaston prism oriented at 45° with respect to the initial polarization to split the beam into two. The split beams were collected by two photodiodes arranged in a differential mode whose output was sent to an SR570 current preamplifier (Stanford research systems). The output of the amplifier was then measured using a lock-in referenced to the chopper frequency. In order to complete the measurements, each photodiode was covered in turn to obtain the total intensity signal. This is used to normalize the previously measured signals that will yield a quantity proportional to the Kerr effect signal (rotation of the polarization angle). Calibration was performed to obtain the actual conversion factor between radians and the normalized signal by tilting the polarizer by a few fractions of a degree and recording the normalized signal.

Figure 1(c) shows MOKE curves (Kerr rotation angle vs magnetic field) for a sample before NiO deposition. The magnetic field was applied perpendicular to the substrate because the easy axis of $Cr_2Ge_2Te_6$ was reported in that direction. For the flakes with the thicknesses more than 5 nm, we observed clear hysteresis. For the flakes with a thickness of 5 nm or less, we did not observe clear hysteresis, which can be attributed to the weaker two-dimensional magnetism[1] and/or to the possibly not-pristine surface or film degradation (e.g., oxidization). After a 20-nm-thick NiO layer was deposited, we measured the same flakes for comparison. These flakes, for the ones that showed a clear hysteresis before the deposition, showed an increase in the coercive field and a change in the hysteresis into a rectangular shape as shown in Fig. 1(d). This clearly indicates the enhanced perpendicular anisotropy induced by depositing the NiO layer.

Importantly, $Cr_2Ge_2Te_6$/NiO not only enhances the perpendicular anisotropy but also increases the Curie temperature. Figure 2(a) shows the temperature dependence of the hysteresis curves in the MOKE signal for the sample shown in Fig. 1 ($Cr_2Ge_2Te_6$ thickness 7 nm, position 2). We characterized the Curie temperature as the midpoint between the temperature in which the coercive field is no longer seen and the one in which we still see a coercive field. For position 2, we observed that the Curie temperature increased by 30 K to ~85 K after NiO deposition. Similarly, we observed an increased Curie temperature to 85 K at position 1 ($Cr_2Ge_2Te_6$ thickness 8 nm), to 70 K at position 3 ($Cr_2Ge_2Te_6$ thickness 6 nm), and to 70 K at position 4 ($Cr_2Ge_2Te_6$ thickness 5.5 nm). For comparison, we measured another sample with 50 nm thickness of NiO, while the thickness of the flake was similar to that of position 2. We observed an even larger increase in the Curie temperature up to 115 K as shown in Fig. 2(b), which is about twice of the Curie temperature on the $Cr_2Ge_2Te_6$ flakes without NiO. In this sample, we also observed further enhanced perpendicular anisotropy as the coercive field was even higher than that of a sample with a NiO thickness of 20 nm.

Figure 2(c) shows the hysteresis of a 202-nm-thick $Cr_2Ge_2Te_6$ flake with NiO of 20 nm. The hysteresis loop at T = 7 K shows small

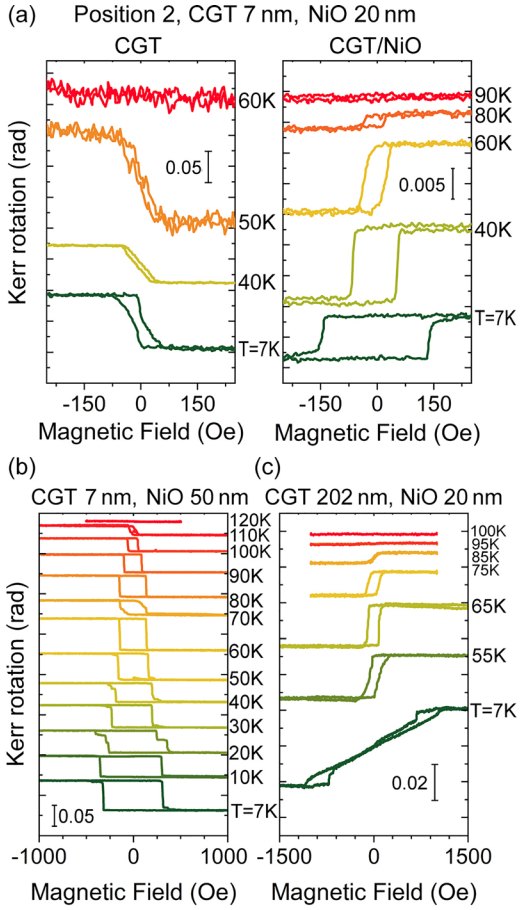

FIG. 2. Temperature dependence of MOKE curves: (a) Comparison for the same flake/position [position 2 in Figs. 1(a) and 1(b)] before and after NiO deposition. The thickness of $Cr_2Ge_2Te_6$ (CGT) is 7 nm, and the thickness of NiO is 20 nm. After NiO deposition, the Curie temperature is increased from ~55 K to ~85 K. (b) The signal measured on a different $Cr_2Ge_2Te_6$ flake with similar thickness but thicker NiO (thickness 50 nm), showing even a stronger increase in Curie temperature to ~115 K. (c) The MOKE signal measured on a relatively thick (202-nm-thick) $Cr_2Ge_2Te_6$ flake with NiO with the same thickness of 20 nm as shown in (a), also showing an enhancement of Curie temperature to ~90 K.

perpendicular anisotropy (coercive field of nearly 0 Oe, similar to that measured in bulk $Cr_2Ge_2Te_6$, see the supplementary material). At elevated temperatures (T = 55 K and above, where ferromagnetism disappears in bulk $Cr_2Ge_2Te_6$ with typical $T_C \sim 60$ K), the hysteresis becomes more rectangular in shape and indicates the presence of some NiO-induced enhancement of perpendicular anisotropy even for such thick flakes. We also raise the possibility in heterostructures of relatively thick $Cr_2Ge_2Te_6$ that we could be accessing to the (different) magnetism of the $Cr_2Ge_2Te_6$/NiO interface [observed in the data above 55 K in Fig. 2(c)] separately from that of bulk $Cr_2Ge_2Te_6$ itself (observed in the data at 7 K). For the case of thin flakes, as exemplified in Figs. 2(a) and 2(b), one likely cannot separate the signal from the $Cr_2Ge_2Te_6$/NiO interface and the bulk $Cr_2Ge_2Te_6$ itself but rather should consider it as the whole $Cr_2Ge_2Te_6$ affected by the interface with NiO.

Figure 3 summarizes the Curie temperatures for $Cr_2Ge_2Te_6$ flakes with various thicknesses, both for those without and with NiO of 20 nm, 35 nm, 50 nm, and 100 nm in thickness together with the data in the literature for $Cr_2Ge_2Te_6$ without NiO.[1,4] The data clearly show that $Cr_2Ge_2Te_6$/NiO can enhance the Curie temperature. For very thin $Cr_2Ge_2Te_6$ flakes (thickness less than 5 nm), we were not able to see a clear enhancement, possibly being attributed to the defective layers (we note that the monolayer is ~0.7 nm according to the crystallographic study[7]). We avoided unnecessarily exposing the samples to air (the exposure time before NiO deposition is typically within five minutes). For thin $Cr_2Ge_2Te_6$ flakes (thickness more than 5 nm and less than 30 nm), the increase in the Curie temperature is strong for the 50-nm-thick NiO. We note different optical constants and the interference effect on Si/SiO_2/$Cr_2Ge_2Te_6$/NiO with different thicknesses of NiO layers, as the color of Si/SiO_2/$Cr_2Ge_2Te_6$/NiO is different (in fact, the substrate color of Si/SiO_2/NiO is also clearly different upon the thicknesses of NiO layers, for example, between 50-nm-thick NiO and 20-nm-thick NiO). In addition, the opposite sign of the MOKE hysteresis curves between Figs. 1(c) and 1(d) is supposedly due to different optical constants.[14] While such a difference in optical constant and interference (giving also different effective optical penetration depths) can affect the MOKE signal (sign and amplitude) due to different NiO thicknesses, it is more difficult to explain the difference in magnetic properties (Tc and anisotropy) of the materials themselves. One of such possible factors would be the difference in crystalline quality and interfaces for different thicknesses of NiO layers. As a controlled experiment to probe this question, we characterized the crystallinity of NiO with different thicknesses for Si/SiO_2/Pt/NiO of 50-nm-thick NiO and 20-nm-thick NiO by X-ray diffraction (SmartLab, RIGAKU Corporation). The (111) and (002) peaks are clearly visible (see the supplementary material for details). The full width half maximum (FWHM) of the (111) peak is 0.60 deg and 0.70 deg for 50-nm and 20-nm thick NiO, respectively. These results were concluded to be the 10–15 nm grain size depending on the details of analysis. The grain size between the two NiO layers of different thicknesses vary only by ~15%. It is not clear presently if the difference in the Curie temperature of $Cr_2Ge_2Te_6$/NiO can be related to this relatively moderate difference in crystallinity. Another possible mechanism might be related to the strain, as we noticed that wrinkles appeared in $Cr_2Ge_2Te_6$ after the NiO deposition. This mechanism could be consistent with the middle panel of Fig. 3, where the thick $Cr_2Ge_2Te_6$ flakes (thickness of more than 30 nm) show little difference in Curie temperature between NiO layers of different thicknesses. For thick $Cr_2Ge_2Te_6$ flakes, we still see the increase in Curie temperature as we discussed in the previous paragraph. The Curie temperature in thick flakes with NiO is higher than that of the bulk Curie temperature reported in various literatures[1,4,7–13] as shown in the right panel of Fig. 3. This higher Tc in the thick flakes could mostly be contributed by the (enhanced) magnetism at the $Cr_2Ge_2Te_6$/NiO interface as we discussed earlier [Fig. 2(c)]. While the precise mechanism of the increase in Curie temperature and the enhancement in perpendicular anisotropy for $Cr_2Ge_2Te_6$/NiO interface magnetism cannot be clear yet at this stage, so far there are a few reports on the correlations between the perpendicular anisotropy and the Curie temperature in other systems. Recently, it has been reported that a two-dimensional magnet with additional perpendicular anisotropy shows an increase in the Curie temperature.[15,16] Bonding between 3*d* electrons in the transition

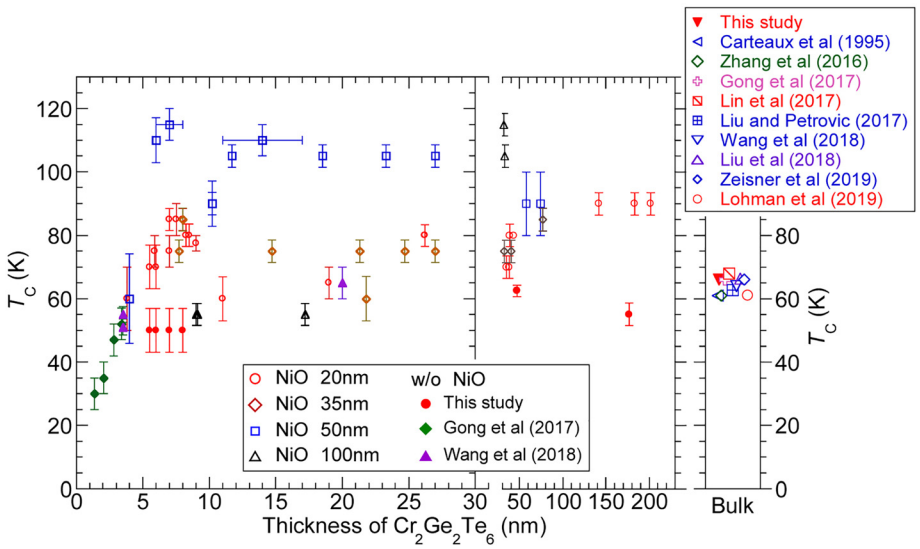

FIG. 3. Curie temperatures measured on $Cr_2Ge_2Te_6$ (closed symbols) and $Cr_2Ge_2Te_6$/NiO (open symbols) with different thicknesses of $Cr_2Ge_2Te_6$ flakes. $Cr_2Ge_2Te_6$/NiO samples show generally higher Curie temperatures than $Cr_2Ge_2Te_6$ over a wide range of thicknesses of $Cr_2Ge_2Te_6$ for 20-nm-thick NiO (open circle) and 50-nm-thick NiO (open rectangle), as well as 35-nm-thick NiO (open diamond) and 100-nm-thick NiO (open triangle). Curie temperatures for $Cr_2Ge_2Te_6$ flakes without NiO are from both this study (closed circle) and the literature (diamond[1] and triangle[4]). The right most panel summarizes the Curie temperatures of bulk $Cr_2Ge_2Te_6$ measured in this study by using a SQUID magnetometer and from the literature (Carteaux *et al.*,[7] Zhang *et al.*,[8] Gong *et al.*,[1] Lin *et al.*,[9] Liu and Petrovic,[10] Wang *et al.*,[4] Liu *et al.*,[11] Zeisner *et al.*,[12] and Lohmann *et al.*[13]). The results show that the Curie temperatures of $Cr_2Ge_2Te_6$/NiO with relatively thick (200 nm) $Cr_2Ge_2Te_6$ still show higher Curie temperature (possibly contributed mostly by the $Cr_2Ge_2Te_6$/NiO interface) than bulk $Cr_2Ge_2Te_6$.

metal and 2*p* electrons in oxygen is known to induce high perpendicular anisotropy for MgO/Fe and MgO/Co from both experimental and theoretical studies,[17,18] which may provide a microscopic mechanism for the enhanced perpendicular anisotropy and increase in the Curie temperature observed in the present studies. We also note that we did not observe any exchange bias (for example reported earlier for the NiO/$Ni_{81}Fe_{19}$ interface[19]) in our hysteresis loop. It is noted that the magnetic field was not applied when we made the interface during the NiO deposition.

In summary, we studied the magnetic properties of a two-dimensional van der Waals magnet and $Cr_2Ge_2Te_6$ flakes covered by NiO thin films by magneto-optical Kerr effects. We characterized the hysteresis loops of $Cr_2Ge_2Te_6$ flakes before and after NiO deposition. $Cr_2Ge_2Te_6$/NiO showed a strong increase in Curie temperature and a clear enhancement in perpendicular anisotropy as evidenced by the increase in the coercive field and the change in hysteresis into a rectangular shape. We observed the Curie temperature as high as 115 K for $Cr_2Ge_2Te_6$/NiO with a NiO thickness of 50 nm, more than twice the one for $Cr_2Ge_2Te_6$ without NiO. The Curie temperature increase for $Cr_2Ge_2Te_6$/NiO is observed for $Cr_2Ge_2Te_6$ with thicknesses ranging from 5 nm to 200 nm. Even $Cr_2Ge_2Te_6$/NiO with 200 nm thick $Cr_2Ge_2Te_6$ flakes showed the higher Curie temperature than bulk $Cr_2Ge_2Te_6$. These results indicate the magnetic properties of two-dimensional van der Waals materials can be controlled by employing the heterostructure and interface with other materials.

See the supplementary material for the hysteresis curve of bulk $Cr_2Ge_2Te_6$ and XRD data of Si/SiO_2/Pt/NiO.

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