Oscillation of coercivity between positive and negative in Mn_xGe_{1-x}:H ferromagnetic semiconductor films*

Qin Yu-Feng(秦羽丰)[a)b)], Yan Shi-Shen(颜世申)[a)], Xiao Shu-Qin(萧淑琴)[a)],
Li Qiang(李 强)[a)], Dai Zheng-Kun(代正坤)[a)], Shen Ting-Ting(沈婷婷)[a)],
Yang Ai-Chun(杨爱春)[a)], Pei Juan(裴 娟)[a)], Kang Shi-Shou(康仕寿)[a)],
Dai You-Yong(代由勇)[a)†], Liu Guo-Lei(刘国磊)[a)], Chen Yan-Xue(陈延学)[a)], and Mei Liang-Mo(梅良模)[a)]

[a)] *School of Physics, National Key Laboratory of Crystal Materials, Shandong University, Jinan* 250100, *China*
[b)] *Department of Applied Physics, School of Information Science and Engineering, Shandong Agricultural University, Taian* 271018, *China*

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Amorphous Mn_xGe_{1-x}:H ferromagnetic semiconductor films prepared in mixed Ar with 20% H_2 by magnetron co-sputtering show global ferromagnetism with positive coercivity at low temperatures. With increasing temperature, the coercivity of Mn_xGe_{1-x}:H films first changes from positive to negative, and then back to positive again, which was not found in the corresponding Mn_xGe_{1-x} and other ferromagnetic semiconductors before. For $Mn_{0.4}Ge_{0.6}$:H film, the inverted Hall loop is also observed at 30 K, which is consistent with the negative coercivity. The negative coercivity is explained by the antiferromagnetic exchange coupling between the H-rich ferromagnetic regions separated by the H-poor non-ferromagnetic spacers. Hydrogenation is a useful method to tune the magnetic properties of Mn_xGe_{1-x} films for the application in spintronics.

Keywords: magnetic semiconductor, hydrogenation, Mn_xGe_{1-x}, antiferromagnetic coupling

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1. Introduction

Spintronics has attracted considerable attention due to its potential application in the next generation information technology. As one of the best candidates for manipulating both charge and spin degrees of freedom in one material, ferromagnetic semiconductors (FMS) have been investigated systematically.[1–16] Intrinsic ferromagnetism, which is desirable for the application of spintronics, has been observed in different kinds of FMS.[6–11] Ohno *et al.*[6,7] reported that (Ga,Mn)As showed a well-aligned ferromagnetic order and anomalous Hall effect with the Curie temperature as high as 110 K. In Fe doped In_2O_3 films, intrinsic ferromagnetism with a strong perpendicular anisotropy was found.[8] The epitaxial single crystal Mn_xGe_{1-x} films have intrinsic ferromagnetism and the Curie temperature increases linearly with increasing Mn concentration.[9] It was also reported that amorphous Ge-based FMS with a high Mn concentration showed intrinsic ferromagnetism.[10,11] However, the origin of the ferromagnetism has been explained by various mechanisms, which are quite different from or even contradictory to each other.

The incorporation of hydrogen has been used to investigate the origin of ferromagnetism in these FMS. It was found that hydrogenated V-doped ZnO powders transformed from paramagnetism to weak ferromagnetism.[12] Yao *et al.*[13] claimed that the hydrogenation enhanced the saturation magnetization, carrier concentration, and Curie temperature of Mn doped amorphous Si:H films by about 500%, 300%–500%, and 100 K, respectively. On the other hand, the ferromagnetic $Ga_{1-x}Mn_xAs$ thin films were found to be paramagnetic after hydrogenation.[14] Moreover, Liu *et al.*[15] found that the magnetization of $Si_{1-x}Mn_x$:B decreased due to the decreased hole concentration after hydrogenation. Theoretical calculations predicted that the Mn-doped single crystal Ge with H interstitials should be a ferromagnetic semiconductor with high Curie temperature and large magnetization. In that case, the H interstitials tend to break the strong antiferromagnetic interaction between the nearest neighboring Mn dopants and force them to have a ferromagnetic spin alignment.[16] Meanwhile, the inhomogeneous distribution of hydrogen was also reported by many groups. Wu *et al.*[17] reported that over 90% of hydrogen was observed to form clusters in less than 10% of the volume in a-Si:H, and the isolated hydrogen accounted for 20–30% of the total volume, which resulted in a major fraction of the volume without hydrogen. The inhomogeneous distribution of H was revealed in hydrogenate amorphous Si by Raman scattering and infrared absorption spectroscopy.[18] It was also reported that the formation of extended planar defects with H_2 molecular originated from the high concentration of hydrogen in Ge, which was detected by high resolution transition electron microscopy and Raman scattering.[19,20]

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†Corresponding author. E-mail: yydai@sdu.edu.cn

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Although the effect of hydrogenation on the magnetic properties of ferromagnetic semiconductors and the inhomogeneous distribution of hydrogen have been discussed,[12–20] it is not clear how the inhomogeneous distribution of hydrogen affects the magnetic properties of FMS in detail. In this paper, we report that the coercivity of Mn_xGe_{1-x}:H thin films changes from positive to negative, and then to positive with increasing temperature. We also provide the inverted Hall loop of $Mn_{0.4}Ge_{0.6}$:H film with negative coercivity at 30 K. The oscillatory coercivity with the temperature is related to the oscillatory exchange coupling between the ferromagnetic regions through nonmagnetic spacers.

2. Experimental details

Mn_xGe_{1-x}:H films were prepared on glass substrates by magnetron co-sputtering from separate Mn and Ge targets. All Mn_xGe_{1-x}:H films were prepared in the atmosphere of mixed Ar with 20% H_2. The substrate temperature was fixed at 20 °C by a water cooling system. The base pressure was better than 3.0×10^{-5} Pa, and it was kept at 1.4 Pa during sputtering. The deposition rate of Mn was fixed at 0.25 Å/s, while the deposition rate of Ge was varied from 0.07 Å/s to 1.85 Å/s. In this way, the concentration of Mn in Mn_xGe_{1-x}:H films could be tuned from 20 at.% to 40 at.%. The substrate was rotated during sputtering to ensure the uniformity of the films. The thickness of all the films was about 300 nm. The amorphous structure and the homogeneous distribution of Mn and Ge elements have been systematically illustrated in our recent paper.[21] The incorporation of hydrogen in Mn_xGe_{1-x}:H films has also been confirmed by infrared absorption spectroscopy.[21] The magnetic properties were measured by a superconducting quantum interference device (SQUID).

3. Experimental results and discussion

Figures 1(a) and 1(b) show the hysteresis loops of $Mn_{0.2}Ge_{0.8}$:H and $Mn_{0.3}Ge_{0.7}$:H films at typical temperatures with the applied magnetic field perpendicular to the film plane. The hysteresis loops were obtained by deducting all the paramagnetic and/or diamagnetic signals from the glass substrate and the paramagnetic Mn atoms. The average ferromagnetic moments per Mn atom are 0.95 μ_B for $Mn_{0.2}Ge_{0.8}$:H and 0.98 μ_B for $Mn_{0.3}Ge_{0.7}$:H at 5 K. These values are much lower than that of a single atomic magnetic moment (5 μ_B), since the neighboring Mn atoms tend to show antiferromagnetic coupling and/or only partial Mn atoms show ferromagnetism and the others show paramagnetism. As revealed in Fig. 1, the saturation magnetization as well as the saturation field of the Mn_xGe_{1-x}:H films decreases with increasing temperature. The ferromagnetism can be observed from the hysteresis loops with coercivities and remanent magnetization.

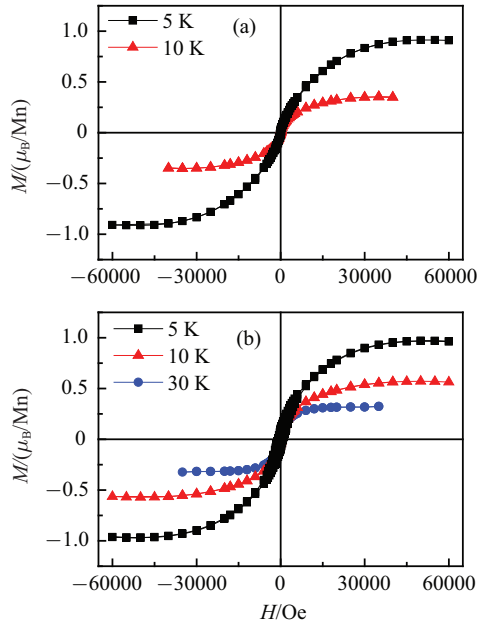


Fig. 1. (color online) Hysteresis loops of (a) $Mn_{0.2}Ge_{0.8}$:H and (b) $Mn_{0.3}Ge_{0.7}$:H films at typical temperatures with the applied magnetic field perpendicular to the film plane.

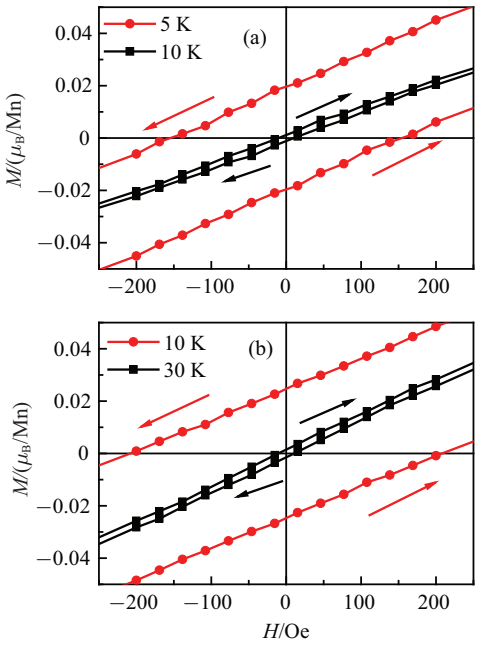


Fig. 2. (color online) The enlarged hysteresis loops of (a) $Mn_{0.2}Ge_{0.8}$:H and (b) $Mn_{0.3}Ge_{0.7}$:H in low fields at typical temperatures shown in Fig. 1. The arrows denote the scanning direction of the magnetic field.

To investigate the details of these hysteresis loops of $Mn_{0.2}Ge_{0.8}$:H and $Mn_{0.3}Ge_{0.7}$:H films illustrated in Fig. 1, the enlarged plots are shown in Figs. 2(a) and 2(b), respectively. From the scanning paths marked by the arrows, it is clear that the switching field (at which the magnetization changes sign) at high temperatures shows a positive value (some researchers call it negative coercivity), which is in strong contrast to the usually observed negative value (positive coercivity) in the normal hysteresis loops at low temperatures. For $Mn_{0.2}Ge_{0.8}$:H, the coercivities are 155 Oe at 5 K and –10 Oe

at 10 K, while for $Mn_{0.3}Ge_{0.7}$:H, the coercivities are 200 Oe at 10 K and –11 Oe at 30 K.

Figure 3(a) shows the magnetic field dependence of magnetization (M–H curves) of $Mn_{0.4}Ge_{0.6}$:H film at typical temperatures with the applied magnetic field perpendicular to the film plane. The $Mn_{0.4}Ge_{0.6}$:H film exhibits ferromagnetism and the saturation magnetization decreases with increasing temperature. However, the coercivity of $Mn_{0.4}Ge_{0.6}$:H film is 1800 Oe at 5 K, –14 Oe at 50 K, and 30 Oe at 150 K. Although the negative coercivity due to the antiferromagnetic coupling has been observed in an exchange-coupled multilayer system,[22–24] granular films,[25–28] and a magnetic semiconductor,[29] the oscillation of coercivity with temperature has not been discovered in FMS and hydrogenated systems yet.

Figure 3(b) shows the magnetization curves of $Mn_{0.4}Ge_{0.6}$:H film in low fields, which are measured by scanning the magnetic field from 60000 Oe to –60000 Oe at different temperatures. From Fig. 3(b), we can see that the coercivity is positive at 20 K, 23 K, 120 K and 150 K, while it is negative at 30 K, 50 K, 80 K and 100 K, which obviously indicates that the coercivity is positive at low temperatures and negative at intermediate temperatures, and then returns to positive again at high temperatures. In other words, the coercivity oscillates between positive and negative with increasing temperature. Figure 3(c) further shows the magnetization curves of $Mn_{0.4}Ge_{0.6}$:H film measured with the applied magnetic field parallel or perpendicular to the film plane at 50 K. It is clear that the magnetization curves measured with the applied magnetic field parallel to the film plane are almost identical with those with the applied magnetic field perpendicular to the film plane. This means that the negative coercivity can be observed for both magnetic field directions. However, for most of the exchange-coupled multilayer systems and granular films,[22,26,28] the negative coercivity can only be observed when the applied magnetic field is perpendicular to the film plane.

Figure 4 further shows the temperature dependence of the coercivity of $Mn_{0.4}Ge_{0.6}$:H film, and the inset of Fig. 4(a) shows the enlargement of the coercivity from 20 K to 150 K. In Fig. 4(a) the oscillation of coercivity between positive and negative with temperature can be seen clearly. We also measured the Hall effect of $Mn_{0.4}Ge_{0.6}$:H film at 30 K when the coercivity was negative. The Hall resistivity ρ_{xy} can be divided into two parts: the ordinary Hall resistivity ρ_{xy}^{0} which is proportional to the applied magnetic field and the anomalous Hall resistivity ρ_{xy}^{a} which is proportional to the magnetization. The magnetic field dependence of the Hall resistivity ρ_{xy} of $Mn_{0.4}Ge_{0.6}$:H film (ρ_{xy}–H curve) at 30 K is shown in Fig. 4(b). The positive slope of the ρ_{xy}–H curve in the high magnetic field region indicates that the carriers in Mn_xGe_{1-x}:H films are p-type, which is consistent with that observed in the Mn_xGe_{1-x} ferromagnetic semiconductors.[9–11] Additionally, figure 4(c) further shows the enlargement of the ρ_{xy}–H curve in the low fields. The inverted Hall loop can be clearly seen from the scanning paths marked by the arrows in Fig. 4(c), which is consistent with the negative coercivity observed. The inverted Hall loop was also reported in amorphous Gd–Co films with negative coercivity.[26]

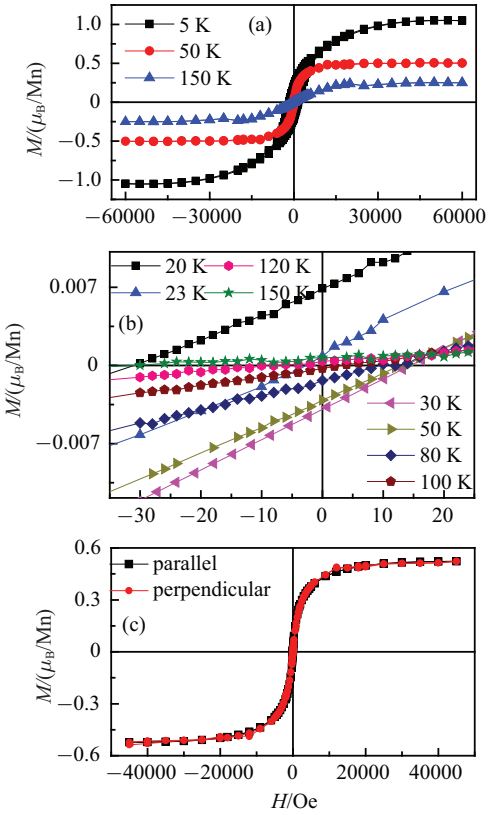


Fig. 3. (color online) (a) Hysteresis loops of $Mn_{0.4}Ge_{0.6}$:H film at typical temperatures with the applied magnetic field perpendicular to the film plane. (b) The enlargement of the magnetization curves of $Mn_{0.4}Ge_{0.6}$:H in low fields, which are measured by scanning the magnetic field from 60000 Oe to –60000 Oe at different temperatures. (c) Magnetization curves of $Mn_{0.4}Ge_{0.6}$:H film measured with the applied magnetic field parallel or perpendicular to the film plane at 50 K.

For the case of positive coercivity at low temperatures, the anomalous Hall resistivity ρ_{xy}^{a}–H loop and the corresponding M–H loop of $Mn_{0.4}Ge_{0.6}$:H film at 10 K are shown in Fig. 5. We can see that the coercivities at 10 K obtained from both curves are identical within the measurement errors. Therefore, the coercivity of Mn_xGe_{1-x}:H films can be confirmed by both methods.

The negative coercivity cannot be found in the conventional ferromagnets, but it can be observed in a ferromagnetic system with antiferromagnetic coupling between neighboring ferromagnetic regions.[22,23,25,29] Now we turn to study the reason why the coercivity of Mn_xGe_{1-x}:H films oscillates between positive and negative with increasing temperature. In our Mn_xGe_{1-x}:H ferromagnetic semiconductor films, the concentration and distribution of Mn and Ge elements can both

be considered as identical for Mn_xGe_{1-x} and Mn_xGe_{1-x}:H films,[21] but the corresponding Mn_xGe_{1-x} films without H do not show negative coercivity. In our previous works, we have confirmed the incorporation of H in Mn_xGe_{1-x}:H films. Therefore, it is reasonable to explain the negative coercivity observed based on the incorporation and the inhomogeneous distribution of hydrogen in Mn_xGe_{1-x}:H films. Although we could not give the direct evidence of inhomogeneous distribution of hydrogen, it can be extrapolated from the experimental results of Refs. [17]– [20].

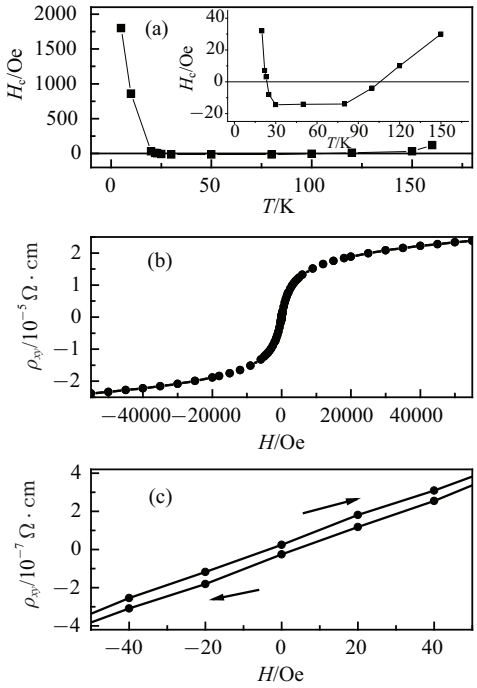


Fig. 4. (a) Temperature dependence of the coercivity of $Mn_{0.4}Ge_{0.6}$:H film. The inset shows the enlargement of the coercivity from 20 K to 150 K. (b) The magnetic field dependence of the Hall resistivity of $Mn_{0.4}Ge_{0.6}$:H film (ρ_{xy}–H curve) at 30 K. (c) The enlargement of the ρ_{xy}–H curve in low fields shown in panel (b), the arrows denote the scanning direction of the magnetic field.

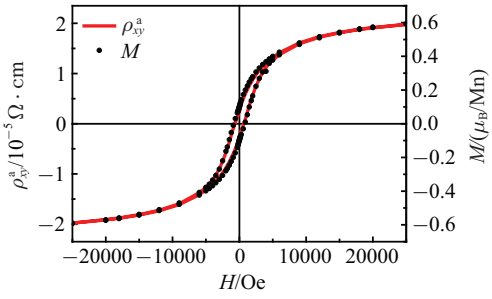


Fig. 5. (color online) Anomalous Hall resistivity ρ^a_{xy}–H loop and the corresponding M–H loop of $Mn_{0.4}Ge_{0.6}$:H film at 10 K. The line and scatters denote the anomalous Hall resistivity and magnetization, respectively.

At low temperatures, the global ferromagnetism is intrinsic with positive coercivity, which originates from the ferromagnetic exchange coupling between the strongly localized spins of Mn 3d electrons mediated by the weakly localized s, p holes due to the Mn partially replacing Ge.[21] With increasing temperature, the concentration of hole carriers in hydrogen rich clusters is high because the hydrogen passivates the dangling bonds of Ge and/or the defects in the Mn_xGe_{1-x}:H film.[21,30,31] In this case, the regions with rich H show intrinsic ferromagnetism with high Curie temperature. However, the H-poor regions may become paramagnetic, and the sizes of the ferromagnetic regions with rich H may decrease. This means that the ferromagnetic regions become smaller as the paramagnetic spacers grow with increasing temperature. Therefore, the neighboring ferromagnetic regions may show antiferromagnetic or ferromagnetic coupling mediated by the hopping carriers thermally activated in the space regions. The ferromagnetic and antiferromagnetic couplings correspond to the positive and negative coercivities, respectively.

The concentration of carriers and the distance between the neighboring ferromagnetic regions are essential for the coupling of the neighboring ferromagnetic regions, which is similar to the interlayer coupling.[22,29,32] Since the concentration of hole carriers and the distance between the neighboring ferromagnetic regions change with temperature, the oscillation from antiferromagnetic to ferromagnetic coupling between the neighboring ferromagnetic regions can be achieved with increasing temperature. So, we can observe that the coercivity of Mn_xGe_{1-x}:H films oscillates between positive and negative with increasing temperature. The materials with negative coercivity can reduce the hysteresis loss, so the inverted magnetization and Hall loops may have advantages in device applications.

4. Conclusion

In conclusion, we find that the amorphous Mn_xGe_{1-x}:H magnetic semiconductor films show the global ferromagnetism at low temperatures, and the paramagnetic regions with poor H are formed with increasing temperature. With increasing temperature, the coercivity of Mn_xGe_{1-x}:H films changes from positive to negative, and then to positive. We also observe the inverted Hall loops of $Mn_{0.4}Ge_{0.6}$:H film at the temperature with which the coercivity is negative.

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