Enhancement of ferromagnetism in polycrystalline $Si_{0.965}Mn_{0.035}$:B films by boron plasma treatment*

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This paper reports that the polycrystalline $Si_{0.965}Mn_{0.035}$:B films have been prepared by cosputtering deposition followed by rapid thermal annealing for crystallization. The polycrystalline thin films consist of two ferromagnetic phases. The low temperature ferromagnetic phase with Curie temperature (T_c) of about 50 K is due to the Mn_4Si_7 phase in the films, while the high temperature one (T_c ∼250 K) is resulted from the incorporation of Mn into silicon. The films are treated by boron plasma excited with the approach of microwave plasma enhanced chemical vapor deposition for 40 minutes. After plasma treatment, it is observed that no extra magnetic phases or magnetic complexes exist in the films, while both the high temperature saturation magnetization and the hole concentration in the films increase. The obvious correlation between the magnetic properties and the electrical properties of the polycrystalline $Si_{0.965}Mn_{0.035}$:B films suggests that the hole carriers play an important role in Si:Mn diluted magnetic semiconductors.

Keywords: magnetic semiconductors, silicon, thin films

PACC: 7500, 8140R, 7280C

1. Introduction

Diluted magnetic semiconductors (DMS) have attracted much attention of researchers because of their potential application in spintronics.[1−5] Since silicon is the most widely used conventional elemental semiconductor, to achieve Si-based DMS is believed to be significant due to the compatibility between spintronic devices and the active electronic devices. However, among the work published on Mn doped Si DMS, the results are inconsistent, even controversial. It was reported that $Si_{1-x}Mn_x$ prepared by ion-implantation technology showed ferromagnetism with Curie temperature ranging from 70 K to 600 K.[6−12] $Si_{1-x}Mn_x$ films fabricated by vacuum evaporation, magnetron sputtering or molecular beam epitaxy have been claimed to exhibit ferromagnetism with Curie temperature around room temperature.[13−16] The mechanism of ferromagnetism in Si-based DMS is also far from well being understood. Bolduc *et al.* believed that the ferromagnetic exchange interaction is hole-mediated[6] while in Kwon's report,[8] the ferromagnetism comes from the interaction between the interstitial and substitutional Mn ions. Later, it was reported that hole carriers play an important role in the ferromagnetism in Si:Mn DMS.[14,16] However, T. S. Chin *et al.* recently reported that ferromagnetism in Si:Mn DMS is attributed to the indirect exchange mediated by localized carriers in the impurity states.[10] More intensive and extensive work is needed for better understanding the mechanism in Si-based DMS.

Plasma treatment is a mature process in modern electronics to change the electrical properties of silicon films. It would also be useful for investigating the relation between the ferromagnetism and free hole-carriers in the Si-based DMS. This article presents the results about the enhancement of the ferromagnetism in polycrystalline $Si_{0.965}Mn_{0.035}$:B thin films by boron plasma treatment.

2. Experiment

The $Si_{0.965}Mn_{0.035}$:B thin films were deposited on single crystalline Si (001) substrates by radio-frequency magnetron sputtering followed by rapid thermal processing for crystallization. The target was a single crystalline Si with boron concentration of 2×10^{15} atom/cm^3 which was partially covered with highly purified Mn chips for incorporation of Mn into the deposited films. With base pressure of 1×10^{-5} Pa, the operation pressure and power were 1 Pa and

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100 W, respectively. The thickness of the samples was fixed at 3 μm. After deposition, the samples were annealed at 1300 °C for 2 min in an Ar ambience with a rapid thermal annealing (RTA) system for crystallization. Then the films were treated in B_2H_6 plasma for 40 minutes at a pressure of 8 Pa using microwave plasma enhanced chemical vapor deposition (MPCVD) approach. During plasma treatment, the films were kept at 200 °C. The concentrations of manganese in the films were detected with field-emission scanning electron microscope (EDAX). The structural properties of the films were analysed through x-ray diffraction (XRD). Superconducting quantum interference device (SQUID) system, MPMS-XL from quantum design, was employed to investigate the magnetic properties of the films. Moreover, the carrier type and concentrations in the films before and after boron plasma treatment were characterized by Hall effect measurement using physical property measurement system (PPMS).

3. Results and discussion

Through EDAX measurement, the Mn concentrations in the films were 3.51% and all the films were p-type determined by Hall effect measurement. Figure 1 shows the experimental results of magnetic properties of the samples before and after treatment. All the data were obtained after subtraction of the diamagnetic contribution from the substrates. Figure 1(a) shows the typical magnetic hysteresis loops of the crystallized films before and after treatment. The loops were recorded at 200 K. It is observed that the crystallized films were ferromagnetic at 200 K and after plasma treatment, the saturation magnetization of films increased significantly. Figure 1(b) is the temperature dependence of the magnetization of the crystallized films before and after treatment at applied field at 1000 Oe (1 Oe = 80 A/m) and the inset shows typical M–T curve of as-deposited films. It is indicated that the films contained two ferromagnetic phase: a low Curie temperature phase (T_c ∼50 K) and a high temperature one with Curie temperature of 250 K. In fact, among all the Si–Mn compounds, besides Mn_4Si_7 whose Curie temperature is 47 K,[17] only MnSi is ferromagnetic and its Curie temperature is about 30 K,[18] and the compounds of boron and manganese i.e. MnB and MnB_2, are ferromagnetic with Curie temperatures of about 306 K and 143 K, respectively.[19,20] Moreover, as shown in the inset of Fig. 1(b), the as-deposited films showed no ferromagnetism in the temperature range measured. This strongly supports that the high temperature ferromagnetism in the crystallized films is caused by the incorporation of Mn into silicon lattice after the post-thermal treatment, which is consistent with the results of the former work.[14] Furthermore, it can be seen from Fig. 1(b) that after treatment, the increase of the magnetization at low temperature is almost the same as that at high temperature. And because the magnetization at low temperature is contributed by the low-temperature phase and high temperature phase, it was believed that little change of magnetization occurs for the low-temperature phase and the boron plasma processing affects the magnetization of the high temperature phase only.

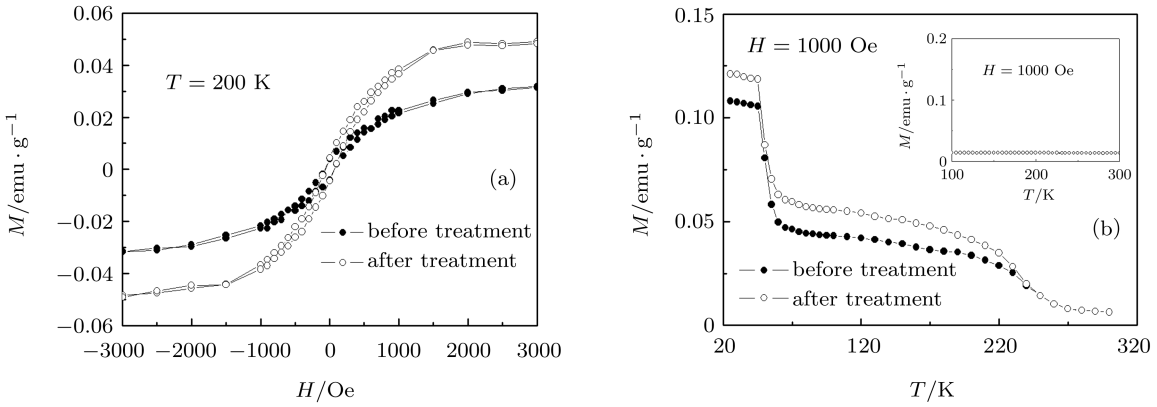


Fig. 1. (a) Typical 200-K magnetic hysteresis loops of the films before and after plasma treatment, respectively. (b) Temperature dependence of the magnetization of the films before and after treatment at applied field of 1000 Oe. Inset shows the typical M–T curve of as-deposited films.

Figure 2 shows the typical XRD spectrum of the crystallized films before and after treatment. Most peaks are due to the structure of silicon while a set of weak peaks marked $*$ belongs to the Mn_4Si_7 phase which causes the low temperature ferromagnetism ($T_c \sim 50$ K).[14,17] Compared with standard spectra of silicon[21] shown in Table 1, we find that the positions of diffraction peaks generally shifted towards lower angles, indicating the lattice expansion in silicon with incorporation of Mn. But the most striking feature indicated in the figure is that both the positions and relative intensity of diffraction peaks changed little after treatment under the detection resolution limit of the technique.

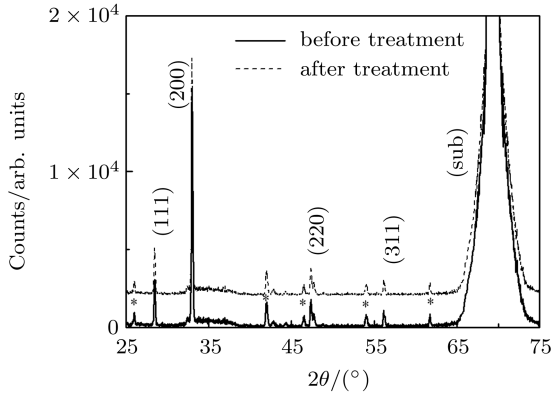


Fig. 2. The XRD spectra of the polycrystalline films before and after boron plasma treatment, respectively.

Figure 3 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization of the films before and after boron plasma treatment as a function of temperature at applied field of 300 Oe. It is observed that a distinct splitting between the ZFC and FC curves in all the samples below 230 K, which is a typical behaviour in DMS.[22−24] While, for nano-particle magnetic system the ZFC and FC curves overlap only at high temperature range and there appears a peak in the ZFC curve since 'blocking' mechanism owes to the competition between the thermal energy and the magnetic anisotropy energy of nano-particles.[25−27] In Fig. 3, besides a peak at low temperature due to the Mn_4Si_7 phase, no signal for the peak can be observed in the ZFC curves at high temperature range. Therefore, it is believed that besides Mn_4Si_7, there are no other magnetic nano-particles existing in all the samples; ferromagnetism at 250 K was caused by the incorporation of Mn into silicon.[14] Moreover, it should also be noticed that the shape of the ZFC and FC curves of all the samples shows no change which gives strong evidence that boron plasma treatment does not cause extra magnetic phases or magnetic complexes.

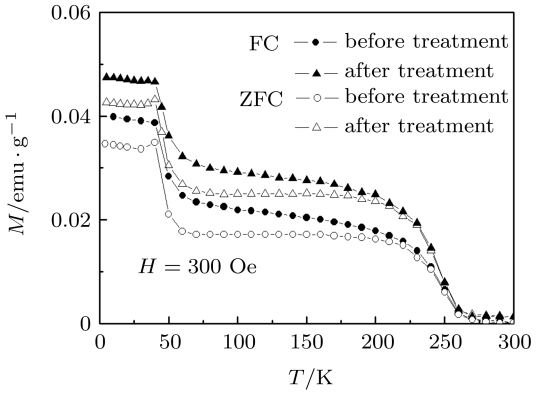


Fig. 3. The zero field cooled (ZFC) and field cooled (FC) M–T curves of films before and after treatment at applied field of 300 Oe.

When we calculate the effective Mn concentration which contributes to the high temperature ferromagnetism, the amount of those formed Mn_4Si_7 phase should be removed. Based on Ref. [17], the magnetization of the Mn_4Si_7 phase is saturated at a magnetic field of 1000 Oe, and the saturation value is found as 0.012 μ_B/Mn. In Fig. 1(b), by extrapolating the M–T curve from 200 K to 100 K, the magnetic moment due to Mn_4Si_7 phase at low temperature is found as 0.0692 emu/g and 0.0689 emu/g for the samples before and after treatment respectively. Therefore, the amount of Mn_4Si_7 phase does not change after boron plasma treatment, which is consistent with the results of XRD analysis. The effective Mn concentration of the high temperature ferromagnetism for all the samples before and after treatment is 0.57%.

Table 1. Comparison of the positions of diffraction peaks of the samples in this work with the standard silicon spectra reported.

peaks		[111]	[200]	[220]	[311]
$2\theta/(\circ)$	standard Si	28.65	33.20	47.66	56.56
	crystalline Si	28.46	33.00	47.38	56.20
	crystalline Si after plasma treatment	28.46	32.98	47.38	56.18

From the above-mentioned discussion, it can be excluded that the enhancement of the high temperature ferromagnetism was caused by any extra mixed magnetic phase after boron plasma treatment. It is reasonable that the magnetization change is interpreted due to the change of free hole-carriers after treatment. It is well known that the energy level induced by boron doping into silicon is shallow acceptor level. For boron doping, hole carriers could be supplied due to their low thermal activation energy. The boron plasma treatment would increase the boron concentration in the films. Thus, the electrical properties of the films would be greatly changed after boron plasma treatment. It is confirmed by Hall effect measurement that after boron plasma treatment, the hole concentration in the films increases from 3.68×10^{15} cm^{-3} to 5.12×10^{15} cm^{-3}. Figure 4 shows the temperature dependence of resistivity of the samples before and after treatment. It is observed that the resistivity of samples decreases after boron plasma treatment, this is consistent with the results from Hall measurements.

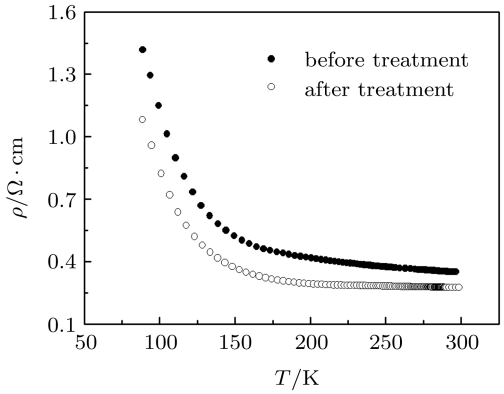


Fig. 4. Temperature dependence of resistivity of the films before and after plasma treatment.

In our work, it was observed that the ferromagnetism in the films is enhanced with the increase of the hole concentration while the Curie temperature is independent of the hole concentration. In the mean-field model,[28,29] the exchange interaction between the local magnetic moments of transition metal is a Ruderman–Kittel–Kasuya–Yosida type indirect exchange and relies on the sp-d exchange between the transition metal states and the free carriers. This model has successfully explained the origin of ferromagnetism in Mn:GaAs where the hole-mediated long range ferromagnetic interaction overcomes the short range antiferromagnetic coupling that occurs in the bulk Mn. In our samples, the hole concentration is much lower than the effective Mn concentration, over two orders. Therefore, it is reasonable to understand that many Mn atoms which have already incorporated into silicon lattice are still isolated because of lacking sufficient hole carriers, similar to the case in Mn doped ZnO.[22] The increase of hole concentration in the films would increase the amount of coupled Mn atoms, leading to higher saturation magnetization. Therefore, it is observed in our work that the saturation magnetization of the high temperature ferromagnetism increases after boron plasma treatment. On the other hand, the Curie temperature is predominantly determined by the strength of the exchange interaction between the Mn impurities. The change of hole concentration only affects the number of coupled Mn atoms, rather than the coupling strength. Therefore, it is observed that only saturation magnetization changes obviously while the Curie temperature of the films does not change. Our results are consistent with the model Dietl *et al.* This work gives strong evidence that the ferromagnetic exchange in Si:Mn DMS is hole-mediated.

4. Conclusion

In summary, we have investigated the structural, magnetic and transport properties of p-type polycrystalline $Si_{0.965}Mn_{0.035}$:B thin films. The hole concentration increases after boron plasma treatment because of the increase of boron dopant in the films. It is observed that the high temperature ferromagnetism is sensitive to hole concentration, which suggests that a hole-mediated ferromagnetism exists in the polycrystalline $Si_{0.965}Mn_{0.035}$:B films.

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