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Effect of hydrogenation time on magnetic and electrical properties of polycrystalline $Si_{0.956}Mn_{0.044}$:B thin films*

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This paper reports that polycrystalline $Si_{0.956}Mn_{0.044}$:B films have been prepared by cosputtering deposition followed by rapid thermal annealing for crystallization. The polycrystalline thin films were treated by hydrogen plasma excited with approach of radio-frequency plasma enhanced chemical vapour deposition for different time of 10 minutes, 15 minutes and 40 minutes. After hydrogenation, the structural properties of the films do not show any change, while both the saturation magnetization and the hole concentration in the films increase at first, then decrease with the increase of hydrogenation time. The obvious correlation between the magnetic properties and the transport properties of the polycrystalline $Si_{0.956}Mn_{0.044}$:B films suggests that a mechanism of hole-mediated ferromagnetism is believed to exist in Si-based diluted magnetic semiconductors.

Keywords: magnetic semiconductor, silicon, magnetism
PACC: 7500, 8140R, 7280C

1. Introduction

Diluted magnetic semiconductors (DMS) are considered as a favourable material to improve the efficiency of spin injection from ferromagnetic materials to semiconductors and have attracted much attention of researchers.[1−5] Silicon is the most widely used conventional elemental semiconductor and has been the backbone of microelectronics industry for decades. To achieve Si-based DMS is believed to be significant due to the compatibility between spintronic devices and active electronic devices. Therefore, in recent years, efforts have focused on fabrication and property investigation of Si-based DMS. Following the report of ferromagnetism with Curie temperature of 210 K in $Si_{0.93}Mn_{0.07}$ films prepared by vacuum evaporation,[6] Zhang *et al* observed ferromagnetism with Curie temperature over 400 K in $Si_{0.95}Mn_{0.05}$ films.[7] Later, using Mn ion implantation technology, both Bolduc *et al* [8] and Bandaru *et al* [9] found ferromagnetism with Curie temperature over 400 K in p-type single-crystal Si. While using ion implantation, Kwon *et al* reported ferromagnetism with Curie temperature only about 70 K in p-type single-crystal $Si_{0.95}Mn_{0.05}$ films.[10] 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[8] while in Kwon's report,[10] the ferromagnetism comes from the interaction between the interstitial and substitution Mn ions. Recently, ferromagnetism with Curie temperature about 250 K has also been observed in $Si_{0.9782}Mn_{0.0228}$:B films prepared by radio frequency (RF) sputtering technique and the mechanism of ferromagnetism is again believed to be hole-mediated.[11] More intensive and extensive work is needed for better understanding the mechanism in Si-based DMS.

Hydrogen passivation is a good method for investigating the origin of ferromagnetism in DMS. Hydrogenation gave strong evidence which proved that the mechanism of ferromagnetism in $Ga_{1-x}Mn_xAs$ films prepared by low temperature molecular-beam epitaxy was hole-mediated.[12] Moreover, Lee *et al* reported that hydrogen induces ferromagnetism in ZnCoO films

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and the enhancement of ferromagnetic spin-spin interaction in the films goes much beyond a carrier-mediated effect,[13] while in Ref.[14], room temperature ferromagnetism observed in hydrogenated Zn-CoO samples prepared by solid state reaction was partially due to the existence of cobalt nanoparticles. Hydrogenation 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 carriers in the Si-based DMS. The results presented in this article are those about the effect of hydrogenation time on the magnetic and transport properties of polycrystalline $Si_{0.956}Mn_{0.044}$:B thin films.

2. Experiment

The $Si_{0.956}Mn_{0.044}$:B thin films were deposited on single crystalline Si (001) substrates by RF magnetron sputtering followed by a rapid thermal processing for crystallization. The target was a single crystalline Si with boron concentration of about 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 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 ambient Ar with a rapid thermal annealing system for crystallization. Then the films were hydrogenated for 10, 15 and 40 minutes in NH_3 plasma at a pressure of 10 Pa using plasma enhanced chemical vapour deposition approach. During hydrogenation, 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 hydrogenation were characterized by Hall effect measurement using physical property measurement system (PPMS).

3. Results and discussion

For the films, a concentration of 4.41% for Mn and hole carriers in the films were determined with EDAX and Hall effect measurement, respectively. Figure 1 shows the experimental results of magnetic properties of the samples with different hydrogenation time. The sample with hydrogenation time of 0 minute is the film before hydrogenation. 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 films at 200 K with different hydrogenation time, the inset shows typical M-H curve of the as-deposited films at 200 K. Figure 1(b) shows the temperature dependence of the magnetization of the films before and after hydrogenation. We observe that the as-deposited samples show no ferromagnetism and after crystallization 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 caused by Mn atom incorporated into silicon lattice, which is consistent with the results of the previous work.[11] However, after hydrogenation, the magnetization of the high temperature ferromagnetic phase (T_c ~250 K) increases at first, then decreases with the increase of hydrogenation time as shown in Fig.1. It also can be seen from

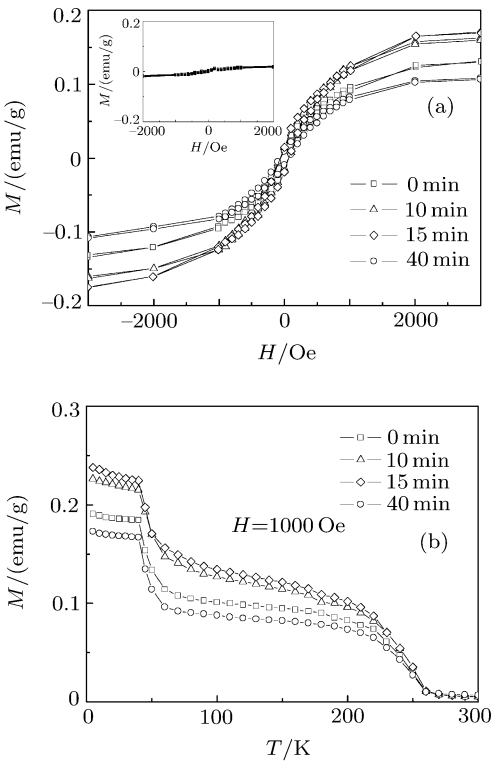


Fig.1. (a) Typical magnetic hysteresis loops of the films with different hydrogenation time at 200 K, respectively. Inset shows the typical M-H curve of as-deposited films at 200 K. (b) Temperature dependence of the magnetization of the films with different hydrogenation time (1 Oe=80 A/m).

Fig.1(b) that the increment of the magnetization at low temperature is almost the same for all the samples, indicating that the hydrogen passivation processing affects the magnetization of the high temperature phase only.

Figure 2 shows the typical XRD spectrum of the crystallized films before and after hydrogenation. 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 ~50 K).[11,15] Comparing with standard spectra of silicon,[16] we find that the positions of diffraction peaks generally shift 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 change little after hydrogenation under the detection resolution limit of the technique.

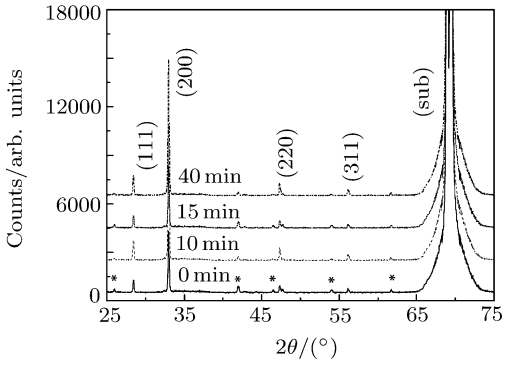


Fig.2. XRD spectra of the polycrystalline films with different hydrogenation time, respectively.

Figure 3 shows the zero-field-cooled (ZFC) and field-cooled (FC) magnetization of the films with different hydrogenation time as a function of temperature at applied field of 300 Oe (1 Oe=80 A/m). We observe that a distinct splitting between the ZFC and FC curves in all the samples below 230 K, which is a typical behaviour in DMS.[17−19] While, for nanoparticle magnetic system the ZFC and FC curves overlap only at high temperature range and there appears a peak in the ZFC curve due to 'blocking' mechanism which owes to the competition between the thermal energy and the magnetic anisotropy energy of nanoparticles.[20−22] 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, we believe that besides Mn_4Si_7, there are no other magnetic nano-particles existing in all the samples; ferromagnetism at 250 K is caused by the incorporation of Mn into silicon.[11] 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 hydrogenation process does not cause any extra magnetic phases or magnetic complexes.

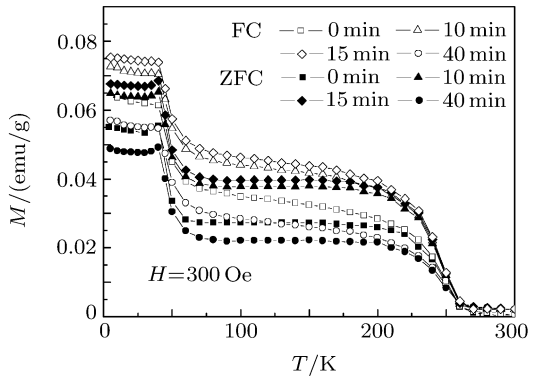


Fig.3. Zero field cooled (ZFC) and field cooled (FC) M–T curves of films with different hydrogenation time at applied field of 300 Oe.

When calculating 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.[15], 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 0.0743 emu/g, 0.0741 emu/g, 0.0739 emu/g and 0.0747 emu/g for the samples with different hydrogenation time of 0, 10, 15 and 40 minutes, respectively. Therefore, the amount of Mn_4Si_7 phase does not change after hydrogenation, 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 hydrogenation is 1.30%.

Both saturation magnetization and hole concentration determined with PPMS are shown in Fig.4(a). We observe that both saturation magnetization and hole concentration increase at first, then decrease with the increase of hydrogenation time. From the abovementioned discussion, it could be excluded that the change of the high temperature ferromagnetism is caused by any extra mixed magnetic phase after hydrogenation. It is reasonable that the magnetization change is interpreted due to the change of carrier con-

centration with the increase of hydrogenation time. As a common process in modern electronics, the effect of hydrogenation on silicon films has been widely studied. Hydrogen passivation served to passivate intragrain and intergrain defects such as dangling bonds in silicon which could 'trap' carriers.[23,24] Therefore it would improve the carrier concentration and mobility in the films, then the resistivity of the films would decrease. On the other hand, hydrogen atoms could form complexes with dopants (i.e. boron and phosphor) after long time hydrogenation resulting in a decrease of acceptor or donor concentration in the silicon.[25−28] In our experiment, in a short hydrogenation time (less than 15 minutes), the effect of defects passivation is dominant, causing the increase of hole concentration. In the case of a long hydrogenation time (longer than 15 minutes), it can be reasonably understood that all the defects have been passivated and the compensation of the H with the dopant of boron becomes the dominant factor which influences the electrical properties of the films. In our work, when hydrogenation time is 40 minutes, it is believed that many boron dopants form complexes with hydrogen atoms. Therefore, the hole concentration is even lower than that of the film before hydrogenation. Figure 4(b) shows the temperature dependence of resistivity of the samples before and after hydrogenation. It is observed that the resistivity of samples decreases at first, then increases with the increase of hydrogenation time, this is consistent with the results from Hall measurements.

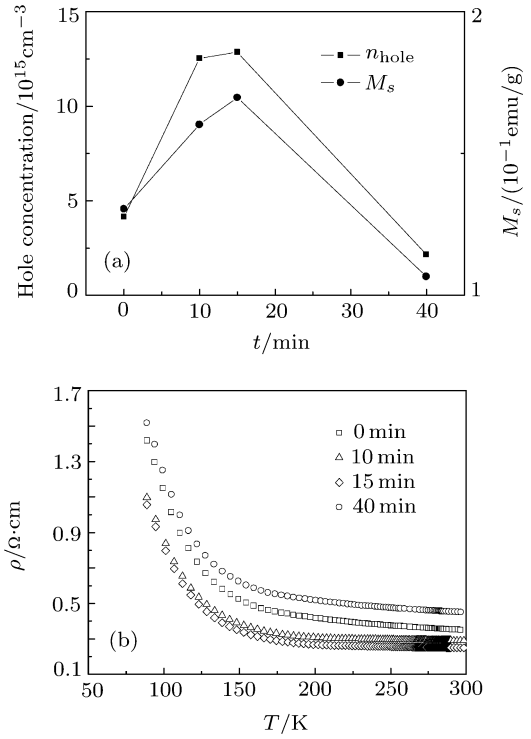


Fig.4. (a) Variation of hole concentration and saturation magnetization at 200 K with the time of hydrogenation. (b) Temperature dependence of resistivity of the films with different hydrogenation time.

In our work, it was observed that saturation magnetization of the films is proportional to the hole concentration while the Curie temperature is independent of the hole concentration. In the mean-field model,[29,30] the exchange interaction between the local magnetic moments of transition metal is a Ruderman–Kittel–Kasuya–Yosida (RKKY) 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. 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.[17] The increase of hole concentration in the films would increase the amount of coupled Mn atoms, leading to higher saturation magnetization. In the same way, the decrease of hole carriers causes the decrease of saturation magnetization of the films. Therefore, we observe in our work that the saturation magnetization of the high temperature ferromagnetism increases at first, then decreases with the increase of hydrogenation time. On the other hand, the Curie temperature is predominantly determined by the strength of the exchange interaction between the Mn impurities. In our work, the change of hole concentration only affects the number of coupled Mn atoms, rather than the coupling strength. Therefore, we observe that only saturation magnetization changes obviously while the Curie temperature of the films does not change. Our results are consistent with both Dietl *et al*'s model and previous work.[10] This work gives strong evidence that the ferromagnetic exchange in polycrystalline $Si_{0.956}Mn_{0.044}$:B thin films is hole-mediated.

4. Conclusion

In summary, the structural, magnetic and transport properties of p-type polycrystalline

$Si_{0.956}Mn_{0.044}$:B thin films with different hydrogenation time have been investigated. The hole concentration increases at first, then decreases with the increase of hydrogenation time, because of the combination of hydrogen with the defects and boron dopant in the films. We observe that the high temperature ferromagnetism is sensitive to hole concentration, which suggests that a hole-mediated ferromagnetism exists in the polycrystalline $Si_{0.956}Mn_{0.044}$:B films.

References

[1] Park J H, Vescovo E, Kim H J, Kwon C, Ramesh R and Venkatesan T 1998 *Nature* (London) **392** 794

[2] Prinz G A 1998 *Science* **282** 1660

[3] Wolft S A, Awschalom D D, Buhrman R A, Daughton J M, Molnar S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1448

[4] Zhu H J, Ramsteiner M, Kostial H, Wassermeier M, Schonherr H P and Ploog K H 2001 *Phys. Rev. Lett.* **87** 016601

[5] Ball P 2002 *Nature* (London) **404** 918

[6] Kim H M, Kim N M, Park C S, Yuldashev S U, Kang T W and Chung K S 2003 *Chem. Mater.* **15** 3964

[7] Zhang F M, Liu X C, Gao J, Wu X S and Du Y W 2004 *Appl. Phys. Lett.* **85** 786

[8] Bolduc M, Affouda C A, Stollenwerk A, Huang M B, Ramos F G, Agnello G and Labella V P 2005 *Phys. Rev.* B **71** 033302

[9] Bandaru P R, Park J, Lee J S, Tang Y J, Chen L H, Jin S, Song S A and Brien J R O 2006 *Appl. Phys. Lett.* **89** 112502

[10] Kwon Y H, Kang T W, Cho H Y and Kim T W 2005 *Solid State Comm.* **136** 257

[11] Liu X C, Wang J F, Lu Z L, Lü L Y, Wu X S, Zhang F M and Du Y W 2006 *J. Appl. Phys.* **100** 073903

[12] Goennenwein S T B, Wassner T A, Huebl H, Brandt M S, Philipp J B, Opel M, Gross R, Koeder A, Schoch W and Waag A 2004 *Phys. Rev. Lett.* **92** 227202

[13] Lee H J, Park C H, Jeong S Y, Yee K J and Cho C R 2006 *Appl. Phys. Lett.* **88** 062504

[14] Wang Y, Sun L, Kong L G, Kang J F, Zhang X and Han R Q 2006 *J. Alloys Compounds* **423** 256

[15] Gottlieb U, Sulpice A, Lambert-Andron B and Laborde O 2003 *J. Alloys Compounds* **361** 13

[16] Yeh C Y, Lu Z W, Froyen S and Zunger A 1992 *Phys. Rev.* B **46** 10086

[17] Jayakumar O D, Salunke H G, Kadam R M, Mohapatra M, Yaswant G and Kulshreshtha S K 2006 *Nanotechnology* **17** 1278

[18] Norton D P, Pearton S J, Hebard A F, Theodoropoulou N and Boatner L A 2003 *Appl. Phy. Lett.* **82** 239

[19] Theodoropoulou N, Febard A F, Overberg M E, Abernathy C R, Pearton S J, Chu S N G and Wilson R G 2002 *Phys. Rev. Lett.* **89** 107203

[20] Seo W S, Jo H H, Kim B, Oh S J and Park J T 2004 *Angew. Chem.* **43** 1115

[21] Gao Y H, Bao Y P, Beerman M, Yasuhara A and Shindo D 2004 *Appl. Phy. Lett.* **84** 3361

[22] Lee Y H, Han T C and Huang J C A 2003 *J. Appl. Phys.* **93** 8462

[23] Pankove J I and Johnson N M 1991 *Hydrogen in Semiconductors (Semiconductors and Semimetals)* Vol. 34 ed. Willardson R W and Beer A C (Boston: Academic)

[24] Nickel N H and Schiff E A 1998 *Phys. Rev.* B **58** 1114

[25] Newman R C 1996 *Mater. Sci. Eng.* B **36** 1

[26] Lightowlers M J, Newman R C and Tucker J H 1994 *Semicon. Sci. Techonol.* **9** 1370

[27] Pankove J I 1992 *Mat. Res. Sypm. Proc.* **262** 367

[28] Johson N M, Herring C and Chadi D J 1986 *Phys. Rev. Lett.* **56** 769

[29] Dietl T, Ohno H and Matsukura F 2001 *Phys. Rev.* B **63** 195205

[30] Jungwirth T, Lee B and MacDonald A H 2001 *Physica* E **10** 153