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Preparation of (SiFe)C DMS Based 4H-SiC Substrate*

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Abstract: A diluted magnetic 4H-SiC has been prepared by implanting Fe ions into the substrate. Its Curie temperature reaches as high as 320K and its technology is compatible with current IC. Moreover, the process includes three annealing steps, named HNH annealing in this paper. Each step during this annealing has been analyzed. Comparisons have been made with different Fe concentrations and experimental results demonstrate that when the concentration of Fe is 0.051, the Curie temperature is the highest. According to measurements, some explanation of this phenomenon is given.

Key words: spintronics; diluted magnetic semiconductor; annealing; Curie temperature
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1 Introduction

Since the discovery of ferromagnetism in diluted magnetic semiconductors (DMS), these semiconductors have attracted a great deal of interest due to their favorable magnetic, magnetooptical, and magneto-electrical properties for application in spin-dependent electronic devices, including magnetic-random access memory, spin-filtering devices, and spin-polarization detectors[1~10]. There are two major criteria for selecting the most promising materials for semiconductor spintronics. First, the ferromagnetism should be retained at practical temperatures (i.e. >300K). Second, it would be a major advantage if there were already an existing technology base for the material in other applications[11].

The most challenging task for broad applications is to find magnetic or diluted magnetic semiconductors that operate at room temperature[8,9]. According to the original Zener model of ferromagnetism to predict T_C exceeding room temperature, wide band gap semiconductors should be the most promising. There are many kinds of wide band gap semiconductors. Among them, GaN and ZnO appear to be the most promising materials with Curie temperature at and above room temperature. Recently, lots of work have focused on them and remarkable progress has been made[6,11].

Besides the above candidates, silicon carbide is also a potential DMS host material for spintronics. Some attempts have already been made to fabricate SiC-based DMS by implanting Mn or Fe ions in high doses. Results imply that it is feasible to engineer wide band gap DMS alloys based on SiC. It has been reported that transition metal (TM = V, Cr, Mn)-doped -SiC represents stable ferromagnetism[12]. Moreover, a system of β-SiC:Cr was reported to show the wide-spin-band gap and a half-metallic property with a magnetic moment of $2\mu_B$, which is a desirable characteristic for spintronic devices. Syvajarvi *et al*.[13] prepared 4H-SiC:Mn DMS with a transition temperature of 160K.

In this paper, samples of 4H-SiC:Fe DMS have been prepared and our process will be introduced.

2 Experiment

Bulk 4H-SiC substrates purchased from Cree were used for all these experiments. They are Al-doped. Concentrations were measured at room temperature to be $10^{16}cm^{-3}$.

First, the semiconductor substrate was cleaned. After the standard RCA cleaning process followed by an HF dip (5% diluted HF solution) for 20s, the samples were directly implanted with Fe into the Si face with the implanted condition of 250keV and dose ranges between 3×10^{16} and $5\times10^{16}cm^{-2}$. The ambient temperature was 300℃ during the implantation to avoid amorphization. The wafers were tilted 7° from the normal to minimize the channeling defect. Following implantation, the samples were annealed.

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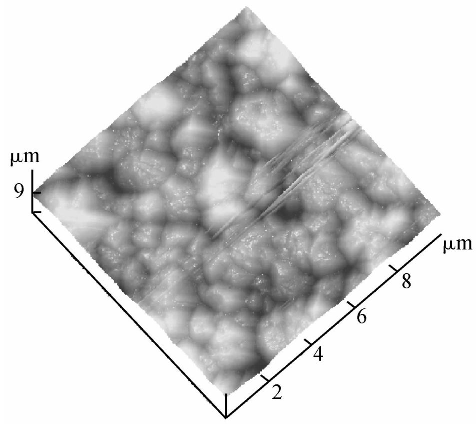

Fig. 1　AFM image of the DMS sample

The annealing technology for DMS here includes three steps: First, annealing in hydrogen atmosphere at 300℃ for 5min, followed by annealing in nitrogen atmosphere at 700℃ for 5min. The last step is annealing in hydrogen atmosphere again at 250℃ for 5min. As far as we know, this annealing technology with three steps is first used in this paper to prepare the 4H-SiC:Fe DMS samples. We name it the HNH annealing process, denoting annealing in hydrogen, nitrogen, and hydrogen, respectively.

Other samples have also been prepared. The process remains the same except for the annealing conditions. The corresponding Curie temperature of different samples will be listed in Section 3.

The annealing tube is a Thermolyne 21100 tube furnace in an ultrahigh flow pure hydrogen and nitrogen atmosphere.

3　Results and discussion

Figure 1 shows the AFM image of the prepared sample. Figure 2 shows the SADP image.

The samples obtained by the process are crystal and can be denoted as $Si_{1-x}Fe_xC$, where x varies from 0 to 0.08. Annealing will be the main method here for increasing T_C of the prepared DMS. Although other researchers' attempts to anneal DMS were not successful, annealing with different steps in different atmosphere seems more promising. The data show that T_C can be significantly increased by the above HNH annealing implanted $Si_{1-x}Fe_xC$ sample.

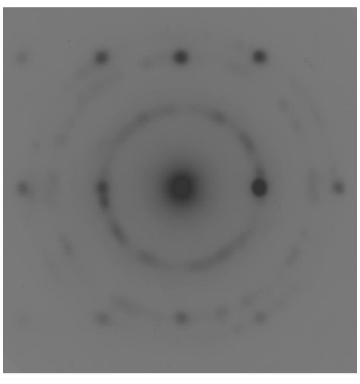
Fig. 2　Selective area electron diffraction pattern (SADP) of the 4H-SiC:Fe DMS sample

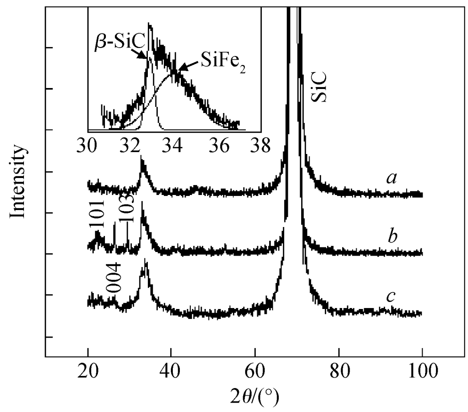

Fig. 3　XRD spectra of the prepared sample corresponding to different annealing stages of the HNH process　(a) Annealing in hydrogen atmosphere at 300℃ for 5min; (b) Based on (a), annealing in nitrogen atmosphere at 700℃ for 5min; (c) Based on (b), annealing in hydrogen again at 250℃ for 5min

The effect of the annealing process of HNH on the structural formation of the sample can be investigated by X-ray diffraction (XRD). XRD is a standard technique for determining structural properties of the prepared sample. This technique provides information such as crystal structure, atomic spacing, and crystal/heterostructure quality. The lattice constant can be determined by Bragg's law, shown as Eq. (1).

$$n\lambda = 2d\sin\theta \qquad (1)$$

where n is the order of the diffraction peak, d is the interplanar spacing, λ is the wavelength of the X-rays, and θ is the incident angle of the X-rays.

Figure 3 shows the XRD spectra of the prepared sample. Curve a corresponds to the sample with only annealing in the hydrogen atmosphere at 300℃ for 5min. Besides the spectrum peak of the substrate SiC, another peak also appears, which corresponds to the $SiFe_2$ aligned in the (112) crystal direction. Thus, the process adopting implantation combined with hydrogen annealing can lead to the crystallization of $SiFe_2$ with a partial micro-crystal structure. The samples undergoing the first annealing step continue to be annealed in nitrogen atmosphere at 700℃ for 5min and the XRD curve is shown as curve b in Fig. 3. Compared with the curve a, there appears to be improvement in the sample's crystallization. The curve c in Fig. 3 corresponds to the sample after the third annealing step, which was carried out in hydrogen at 250℃ for 5min. The intensity of $SiFe_2$ has been improved, showing that the annealing process can help

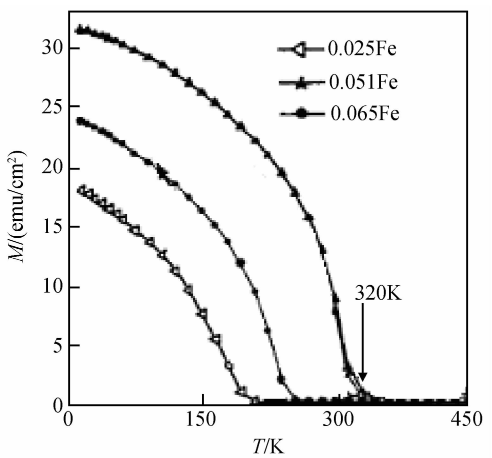

Fig.4 Magnetization as a function of temperature in a 50Oe field for several different Fe concentrations

the crystallization of $SiFe_2$. From the curve c, the peak on the $SiFe_2$ (112) direction is enhanced, while the (211) peak is decreased. At the same time, a new peak for $SiFe_2$ (004) appears. Thus, the third step can help the reconstruction of the elements in the sample and the Fe silicide with improved quality has been grown. The intensities of the Fe silicide peaks are all low compared with the SiC main peak. This may contribute to the thin implanted layer. The inset figure in Fig. 3 is the partially amplified image of the curve c. From the inset, not only the $SiFe_2$, but the cubic SiC appears too. Cubic SiC can also be called β-SiC. After the Fe atoms crystallize with the silicon atom, the relish carbon atom can be reconstructed with a silicon atom to form a new type of silicon carbide crystal. This is the first time the authors observed this crystal change between α-SiC and β-SiC. This can not be observed until the second stage. The third stage of annealing, in hydrogen again at 250℃ for 5min, can be helpful for the reconstruction of silicon carbide crystal.

Figure 3 shows that an epitaxial layer of ferromagnetism layer can be formed by using implantation technology. The 4H-SiC peak always remains the same, showing that implantation with careful angle selection is feasible for the preparation of the sample, without worrying about the crystal damage.

After the best annealing HNH process was fixed based on the above analysis, authors then proceeded to anneal the implanted samples with different Fe concentrations for different implant doses. The Fe fraction x of the investigated samples are $x = 0.025$, 0.051, and 0.065, respectively. A Quantum Design RF SQUID performed all the magnetization measurements in this paper. As shown in Fig. 4, from the relation curve of the magnetization as a function of temperature in a 50Oe field for the samples, the best result of the T_C, 320K, corresponds to that with a Fe concentration of 0.051. The samples with 0.025Fe and 0.065Fe both displayed a dropping tendency for T_C.

According to Fig. 4, among the three different Fe sample concentrations, the sample with 0.051Fe has the best characteristic in the magnetization curve. The three curves in Fig. 4 have the same tendency. Comparing the 0.025 and 0.051 samples, the magnetization is more significant for larger concentrations of Fe. But when the comparison is made between the 0.051 and 0.065 samples, larger concentration corresponds to less T_C. Thus, for samples made by implantation, a 0.051 concentration of Fe is best.

As-prepared samples have a linear drop in the magnetization as temperature increases, which can be attributed to multiple exchange interactions. The tendencies of the three curves in Fig. 4 remain the same, and the interactions remain the same.

The origin of the ferromagnetic behavior in these samples is not clear. Fe being a spherical volume of 2nm radius would imply a superparamagnetic transition temperature of a few Kelvin, the characteristic of high Curie temperature, as shown in Fig. 4, can not be attributed to superparamagnetism. We have observed the secondary phase formation involving the formation of $SiFe_2$ compounds as shown in the inset of Fig. 3. Moreover, a new type of cubic SiC transferring from 4H-SiC also appears as the result of HNH annealing.

To investigate the structure of the samples and the influence of Fe atoms on the material, RBS measurements have been carried out and the results are shown in Fig. 5.

According to this figure and based on calculations, we conclude that a buried layer of 30nm has formed 19nm from the surface. For Fig. 5(a), corresponding to the sample with 0.025Fe, the Fe concentration in $SiFe_2$ is 60%. For the sample with 0.051Fe, the Fe concentration is 66%, indicating that the quality of crystallization when the Fe content is 0.051 is better than other conditions. For the sample with 0.065Fe, the Fe content is higher than 72%. So, we conclude that when the content of Fe is 0.051, the crystallization of the sample is the best.

Since the Curie temperature is expected to be a strong function of both the Fe concentration and the hole density, it is the positional disorder of interacting spins and carriers in doped DMSs that give rise to a distribution of exchange couplings between Fe ions and holes. Since the sample with 0.051Fe shows a similar magnetic behavior to those with other concentrations, the decrease in Curie temperature relative to the 2.5at.% Fe implanted SiC sample may be due to a

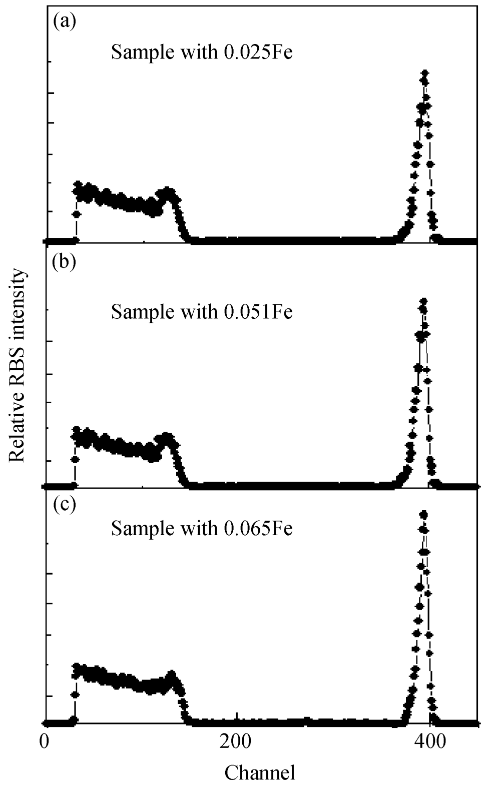

Fig. 5　RBS spectra for samples with different Fe concentrations

lower hole concentration as a result of more residual implant-induced donor levels. Figure 6 shows the capacitance-voltage measurements of samples with 0.051Fe and 0.025Fe. The hole concentration of the sample with 0.051Fe is estimated to be $6\times10^{15}\mathrm{cm}^{-3}$. However, for the sample with 0.025Fe, its hole concentration is $1.3\times10^{15}\mathrm{cm}^{-3}$. So, the different hole concentrations for different samples explain the variable Curie temperature in Fig. 4.

If the concentration of Fe is more than 0.051Fe, antiferromagnetism will appear and its appearance could explain the decrease in the Curie temperature. So, for the sample with 0.065Fe, its Curie temperature

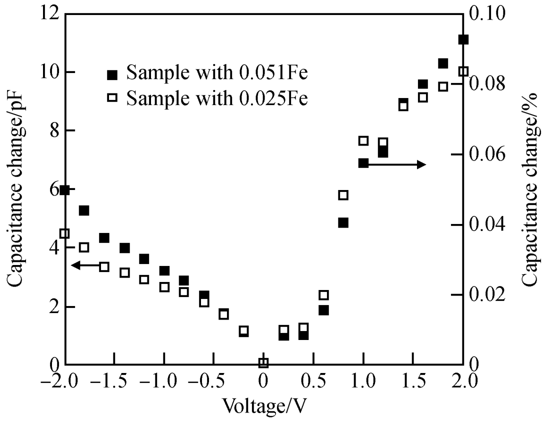

Fig. 6　Curves of capacitance-voltage corresponding to different Fe concentrations

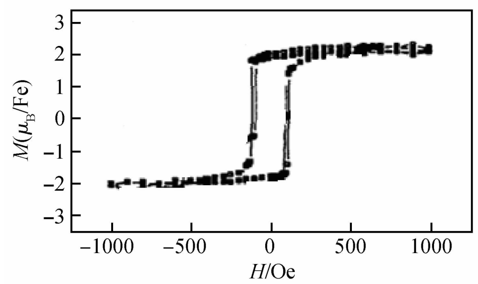

Fig. 7　Hysteresis loops of $Si_{0.95}Fe_{0.05}C$ in different orientations with respect to the applied field at $T=200\mathrm{K}$

shows a decreasing tendency. As a result, the sample with 0.051Fe can be considered as the optimum concentration.

For the sample with 0.051Fe concentration, hysteresis loops were performed with the applied field in-plane orientation as shown in Fig. 7 at $T=200\mathrm{K}$. The magnet field was degaussed before testing. Besides the in-plane field measurement, other orientations have been tested, but they are not shown in Fig. 7. The orientations with the applied field in-plane were found to be easy axes, while the orientation with the applied field normal to the surface was found to be a hard axis. Orientations within the plane show slightly harder magnetic axes in certain directions due to anisotropy. Figure 7 shows that the magnetic character of the sample reveals the Fe atoms in SiC act ferromagnetically at 200K. According to the RKKY theory of super-interchange action[1], a local spin action is supported by the implanted Fe ions. The magnet originates from a super interchange action between magnetic ions. So, magnetism will appear in DMS material. This figure shows the sample with wide-spin-band gap and a half-metallic property with a magnetic moment of $2\mu_B$.

4 Conclusion

In this paper, the wide band gap semiconductor 4H-SiC has been studied for its property of diluted magnetic semiconductor when Fe atoms have been introduced. The Fe atom is implanted into the substrate. After implantation, a careful annealing has been made, including three steps with different atmospheres, temperatures, and times. Based on the result of the XRD spectrum, $SiFe_2$ emerged after the first annealing stage. After the third stage of annealing, a cubic SiC can be observed, which means that after the Fe atoms were introduced into the SiC, a new reconstruction of the SiC molecule occurred.

The magnetization has been measured with different Fe content. A mediated concentration of Fe with 0.051 is the best among all the samples and T_C

has been measured as high as 320K, above room temperature. Moreover, the hysteresis loop of $Si_{0.95}Fe_{0.05}C$ has been measured at $T = 200K$. The result indicates that the DMS sample has a good ferromagnetic character.

Because the implantation is compatible with integrated circuit technology, the method introduced here will have potential application in applying the DMS material at room temperature.

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基于 4H-SiC 衬底的(SiFe)C 的稀磁半导体材料制备*

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摘要：研究了基于 4H-SiC 衬底的(SiFe)C 的稀磁半导体材料制备方法，不同于其他人采用的 MBE 或 MOCVD 生长的方法，用离子注入的方法进行材料制备，能够与现有的集成电路工艺相兼容，用这种方法所对应的样品的居里温度 320K，高于室温，具有潜在应用的价值. 在制备过程中，采用了 HNH 退火工艺，即退火分为三个阶段，每个阶段对应不同的退火气氛、时间和温度，XRD 分析表明，每个阶段都对应不同的结晶结果. 另外，对应不同的 Fe 离子浓度，进行了实验对比，结果表明，当 $x = 0.051$ 的情况下对应最高的居里温度.

关键词：自旋电子学；稀磁半导体；退火；居里温度

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