Journal of Alloys and Compounds 503 (2010) 6–9

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Room-temperature ferromagnetism in Si–SiO_2 composite film on glass substrate

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ARTICLE INFO

Article history:
Received 24 November 2009
Received in revised form 27 April 2010
Accepted 29 April 2010
Available online 6 May 2010

Keywords:
Room-temperature ferromagnetism
Si–SiO_2 composite film
Volume percentage
Defects
Coupling

ABSTRACT

Room-temperature ferromagnetism (FM) has been observed in Si–SiO_2 amorphous films grown on glass substrates. The magnetic moment was largest in the case of the Si–SiO_2 thin film with a Si volume percentage of 16 vol%. The Si content also impacts the magnetic order of the film, and distinct domains were detected in our films. The delicate difference in the M (H) curve between the cases where thermal annealing was carried out in O_2 and Ar atmosphere indicates that the observed ferromagnetism does not originate primarily with oxygen defects. It was concluded that the ferromagnetism arose due to direct coupling between defects. These defects come from the interface between the Si particles and the SiO_2 matrix. By tuning the Si content in the thin films, one can change the defect density and thereby control the strength of the ferromagnetic coupling.

1. Introduction

Much attention has recently been given to magnetic semiconductors based on group IV compounds (mainly Si, Ge) where ferromagnetic coupling arises through incorporation of magnetic impurities, mainly Mn, into the semiconductor matrix. These materials are particularly attractive due to their integration of desirable optical, electronic, and magnetic properties into one single material and the availability of high-quality Si in large sizes at relatively low costs [1–6]. Based on the Zener model, Dietl et al. predicted the appearance of a carrier mediated ferromagnet when Si is doped with 5 vol% Mn [7]. Zhou et al. also indicated that magnetic properties in Mn-implanted p-type Si could be assigned to $MnSi_{1.7}$ nanoparticles [8]. Zhang et al. reported on the crystalline $Mn_{0.05}Si_{0.95}$ alloy with a Curie temperature as high as 400 K [9]. Other transition metals, Co and Mn, co-incorporated into Si based semiconductors were also found to yield ferromagnetic compounds [10]. However, there are disadvantages associated with DMSs, such as the low solubility of the magnetic impurities in the semiconducting matrix and the rather low ferromagnetic ordering temperatures (T_C) achieved so far.

In 2007, Kopnov et al. for the first time observed the magnetic properties of silicon/silicon oxides interfaces [11]. They concluded that the collective orbital magnetism initiated by charge transfer between the substrate and the thin layer caused the observed magnetic moment. Subsequently, interface ferromagnetism was observed in co-doped zinc oxide films [12]. The observed ferromagnetism was associated with neither magnetic precipitates nor contamination, but originated with the silicon/silicon oxide interface. In 2009, Grace et al. pointed to iron contamination as a source for the magnetism in etched silicon [13]. These works may open the way for using room-temperature silicon-based materials as a magnetic material, a possibility that has enormous technological implications.

In this work, to further investigate the ferromagnetic mechanism related to Si-based semiconductors, SiO_2 samples embedded with various percentages of Si were prepared using radio frequency (RF) sputtering. The structure, morphology and ferromagnetism of the films were studied in detail.

2. Experimental details

Si–SiO_2 films were deposited on glass substrates by RF sputtering of high purity SiO_2 target (purity 99.999%) with additional chips of high purity Si also attached to the target. Prior to the deposition process, the background vacuum was reduced to below 6×10^{-4} Pa. The sputtering pressure was 2 Pa with the RF sputtering power being 150 W. By changing the amount of Si in the chips on SiO_2 target, we obtained a series of Si–SiO_2 films with different Si volume percentages. All of the Si–SiO_2 films were 500 nm thick. The samples were annealed in an Ar atmosphere at different temperatures and for different durations. For comparison, series of samples were also annealed in an O_2 atmosphere.

The structures of the films were investigated by X-ray diffraction (XRD) using a “X'Perd PRO”-type diffractometer with a Cu Ka source. The magnetic properties of the Si–SiO_2 films were measured using a PPMS-6000 system. Energy dispersive X-ray spectrometry (EDS) was used to analyze the composition of the samples. Atomic force microscopy (AFM, Nanoscope IV) and magnetic force microscopy (MFM) measurements were used to investigate the morphology and magnetic domain structures of the sample, respectively. Fourier transform infrared spectra (FTIR) were measured on a Nicolet 380 infrared spectrometer.

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doi:10.1016/j.jallcom.2010.04.226

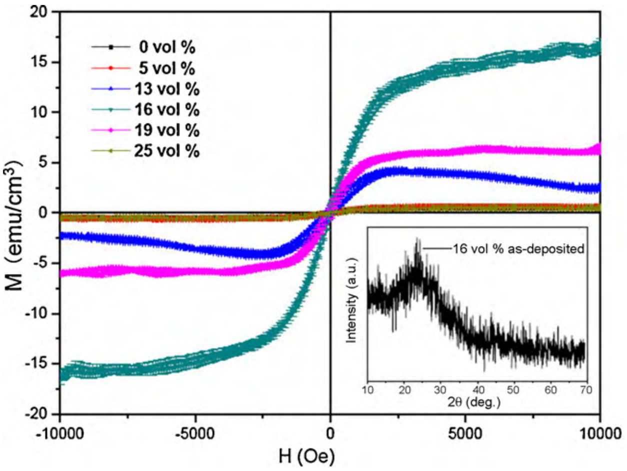

Fig. 1. In-plane hysteresis loops for the Si–SiO$_2$ films with various Si content at room temperature. Each point represents the mean value from three times measurements. The inset shows the XRD patterns of the film with a Si content of 16 vol%.

3. Results and discussion

The magnetization as a function of magnetic field for the as-deposited films with various values for the Si content is displayed in Fig. 1. One can see that the ferromagnetism of the films reaches a maximum of about 16.4 emu/cm^3 when the Si content is 16 vol%. The large magnetic moment is hard to attribute to any kind of impurities. The saturation magnetization increased with increasing Si content up to 16 vol% for our films. However, with further increases in Si content, the ferromagnetism weakened. It is worthwhile to highlight that no ferromagnetism could be observed in the glass substrates (shown in Fig. 2). The EDS spectrum shows that the film consists of Na atoms from the glass substrate plus Si and O, as shown in the inset of Fig. 2. None of these elements is ferromagnetic. This indicates that the magnetism in our films does not result from ferromagnetic impurities. The inset in Fig. 1 shows the XRD patterns for the film with a Si content of 16 vol%. The films were amorphous. The broad bulge located around 23° was attributed to the glass substrate.

To illustrate the origin of ferromagnetism in the films, the morphology image (ai, i = 1, 2, . . ., 5) and the corresponding magnetic domain images (bi, i = 1, 2, . . ., 5) of the samples are shown in Fig. 3. For the film with a Si content of 16 vol%, Si particles were uniformly distributed in the SiO$_2$ matrix and distinct ordered magnetic domains were observed. If the Si content is too high or too low, no evident domains appear. When the Si content is 5 vol%, large Si particles form, but they are far apart. When the Si content is 25 vol%, the film becomes continuous. The films with Si content in the range 13–19 vol% show ferromagnetism. These results demonstrate that the magnetic order of the film correlates with the Si content and the distribution of Si particles.

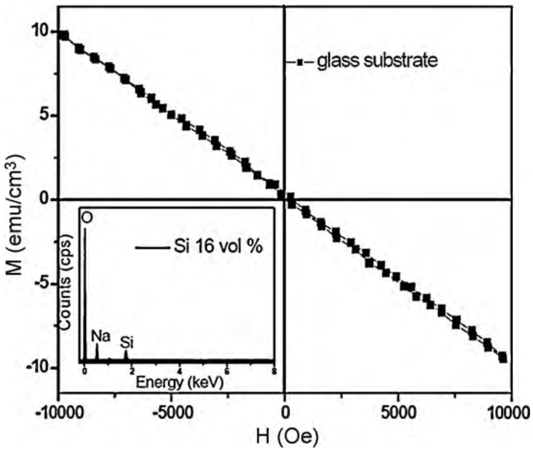

Fig. 2. Room-temperature hysteresis loop for the glass substrate. The inset shows the EDS spectrum from the film with Si content of 16 vol%.

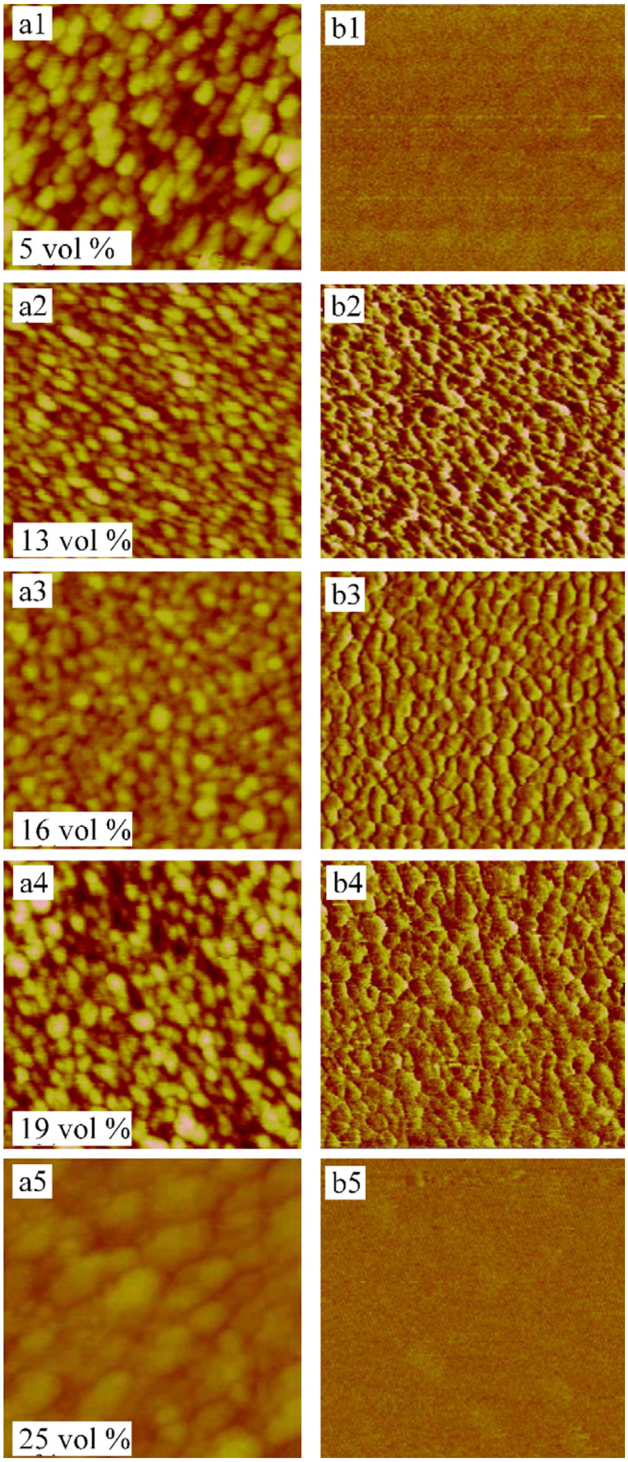

Fig. 3. AFM and MFM images of the Si–SiO$_2$ films with various Si contents. All images show a 2 μm × 2 μm area.

Recently, investigations of a number of undoped metal oxide systems have shown that ferromagnetism may arise from exchange interactions between localized electron spin moments resulting from oxygen vacancies. Oxygen vacancies may lead to n-type dop-

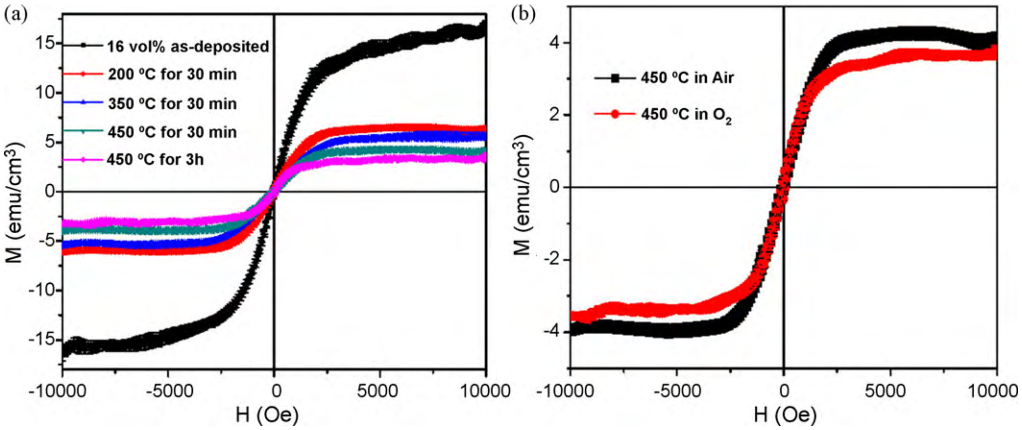

Fig. 4. Room-temperature hysteresis loops for the films with a Si content of 16 vol% annealed (a) at different temperatures and durations in Ar atmosphere and (b) in Ar and O_2 atmosphere at the same temperature and duration. Each point represents the mean value from three measurements.

ing of the material, occupy large Bohr orbital and tend to form an impurity band [14–16]. To explore the effects of oxygen defects on the ferromagnetism of our films, the samples were processed with thermal annealing in either Ar or O_2 atmosphere at different temperatures for various times. The room-temperature hysteresis loops for the Ar annealed films with a Si content of 16 vol% are displayed in Fig. 4a, along with the data for the corresponding as-deposited film. The background diamagnetism arising from the substrate has been subtracted. It was noted that annealing in an Ar atmosphere reduced the saturated magnetization (M_s) of the films significantly. Higher annealing temperatures and longer durations reduce the ferromagnetic signal of the films to the greatest extent. For the sample annealed at 450 °C for 3 h, the M_s is 3.3 emu/cm^3, while the M_s of the as-deposited film is 16.4 emu/cm^3. From Fig. 4b, one can see that, after annealing in an O_2 atmosphere at 450 °C for 30 min, the M_s of the film decreased slightly as compared with that of the sample annealed in Ar atmosphere under the same conditions. With annealing in an O_2 atmosphere, more oxygen vacancies are filled, which degrades the magnetic moments of the films. There are, however, only delicate changes in the $M(H)$ curves for the films annealed in Ar and O_2 atmospheres, and we speculate that oxygen vacancies are not the dominant source of ferromagnetism in Si–SiO_2 composite films, and that there must be another FM source rather than oxygen vacancies.

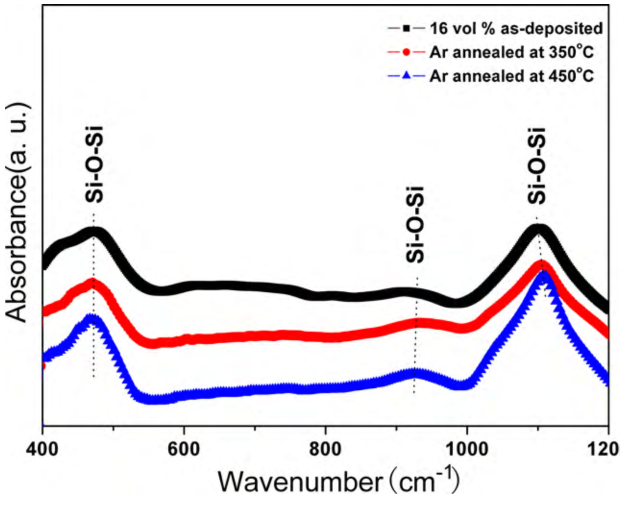

Fig. 5. FTIR spectra of the samples with 16 vol% Si content for the as-deposited and Ar annealed states.

The FTIR spectra are shown in Fig. 5 for the as-deposited and Ar annealed films. Here we have chosen to show data for the film with a Si volume percentage of 16 vol% as it gives the highest magnetization. The 460, 917 and 1099 cm^{-1} bands belong to the Si–O–Si rocking, Si–O–Si bending vibrations and Si–O–Si stretching modes of non-stoichiometric SiO_x, respectively [17]. An increase in the annealing temperature raises the system energy, which makes the Si–O–Si stretching bands of SiO_x shift to higher wavenumbers and increases the peak intensity. The number of isolated Si particles also decreases at higher temperatures and more Si–O–Si form. As a result, the extent of the interface between the Si particles and the SiO_2 matrix decreases. This leads to reduced FM in the annealed films, which is consistent with the magnetic properties results of Fig. 4a.

The question then arises as to the source of the magnetism in our samples. Taking into account the delicate differences between the magnetic characterizations for the films annealed in Ar and O_2 atmospheres and the structure of the Si/SiO_2 films, there are two sources for the magnetism that one might consider: (i) the oxygen vacancies (already discussed above) and (ii) defects arising from the Si content in the films. For our films, the wide range in the Si content leads to various Si particle distributions, and hence defect densities, in the SiO_2 matrix, which, in turn, can influence the magnetic ordering of the samples. When the Si content is less than 16 vol%, the isolated Si particles are relatively far apart, and the lower defect density arising from the interfaces between the Si particles and SiO_2 matrix induces only weak FM coupling. The magnetic coupling reaches a maximum when the Si content is 16 vol%. At this concentration, the defect density is high, so that a strong coupling between the defects will occur. When the Si content exceeds 16 vol%, the Si particles becomes continuous and fully amorphous, which brings the defect density reduced and weakens the magnetic coupling in the film. These results can be confirmed from the AFM and MFM images (Fig. 3). Therefore, direct coupling among defects at the interface between Si particles and the SiO_2 matrix is thought to be the main source of ferromagnetism in our films. It should be emphasized that the results here for ferromagnetic defects in Si–SiO_2 films obtained by reactive sputtering are different from the paramagnetic defects observed in the Si–SiO_2 system prepared by Si thermal oxidation in oxygen [18–20].

4. Conclusions

The FM observed in Si–SiO_2 amorphous films grown on glass substrates is intrinsic. The saturation magnetization reaches a maximum of 16.4 emu/cm^3 when the Si content is 16 vol% for our films. The delicate difference between the results obtained with thermal annealing in O_2 and Ar atmospheres indicates that oxygen defects are not the main source of ferromagnetism in these films. The defects located at the interface between the Si particles and the SiO_2 matrix directly couple and can induce ferromagnetism. Regulating the Si content in the film can change the interface defect density, and thus control the strength of the ferromagnetic coupling.

Acknowledgements

This work was supported by National Science Foundation of China (10804026 and 10774037), Natural Science Foundation of Hebei Province (E2007000280) and Foundation of Hebei Educational Committee (2006123).

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