Structural and Magnetic Properties of Fe-Diluted Si Alloy Films by Pulsed-Laser Deposition

Jooyoung Suh, Kyung Su Lee, Sang Woo Pak, and Eun Kyu Kim*

Department of Physics, Hanyang University, Seoul 133-791

(Received July 10, 2012, Revised September 21, 2012, Accepted September 24, 2012)

Fe-diluted Si alloys grown on p-type Si (100) substrates by pulsed-laser deposition method were studied for structural, electrical, and magnetic properties. The X-ray diffraction patterns for these alloy samples showed a few of peaks with cubic structures such as FeSi, Fe3Si, and Fe4Si. The Fe-composition in alloys are confirmed as Fe atomic percent about 1.25∼6.49% from energy dispersive spectroscopy measurement. The resistivity as a function of the reciprocal temperature was indicated an exponential increase with two activation energies of 5.21 and 7.79 meV. The maximum value of the magnetization at 10 K was about 100 emu/cc, and the ferromagnetism was also observed until 350 K from total magnetization as a function of temperature with applied magnetic field of 3,000 Oe.

Keywords : Fe-diluted Si, Ferromagnetism, Pulsed-laser deposition, Diluted magnetic semiconductor

I. Introduction

New functional properties such as magneto-electric phenomena are expected by a coexistence of electron charge and electron spin in a material. There are unique properties of electron spin as well as electron charge degree of freedom, simultaneously. Spintronics, are an emerging technology to overcome some of physical limitations on electronics, based on Si has accomplished beyond the past few decades [1–5]. It is possible that a next generation spin device based on Si apply to an enhancement of the data storages, transmission speed, etc. In order to improvement theses physical properties, the alloying technology which is one metal with other metals or nonmetals often enhances its properties has been attracted. The physical properties, such as density, reactivity, Young’s modulus, and electrical and thermal conductivity, of an alloy may not differ greatly from those of its elements but engineering properties such as tensile and shear strength may be essentially different from those of the host materials [6–8].

The manipulation of electron spin in semiconductors with transition metals is very important. The efficiency of electron spin injection is still deficient in major problems as low as a few % for the realization of spin field effect transistors, which is contributed by the conductance mismatch of junctions between metal and semiconductor. Diluted magnetic semiconductor (DMS) is known to be a useful way to
overcome the conductance mismatch [9–11]. Group IV–based DMS was concerned to many researchers about structural, electric, magnetic properties, Curie temperature of Mn_{x}Ge_{1−x} is found to increase with \( n_{Mn} \) by molecular beam epitaxy up to 116 K [12]. \( Mn_{0.05}Si_{0.95} \) grown by evaporation method is published with 400 K of Curie temperature. Especially, for Fe–doped Si at both concentrations of 3.125 and 6.250%, only in the nearest atoms range can the ferromagnetic state exist [13].

In this study, the Fe–diluted Si alloy films were grown on p–type Si substrate by pulsed–laser deposition method. The structural, electrical, and magnetic properties of the samples were analyzed by FE–SEM (field emission–scanning electron microscopy), EDS (energy dispersive spectroscopy), and SQUID (superconductor quantum interference device) measurements.

II. Experimental

The Fe–diluted Si alloys were grown on p–type Si (100) substrates by pulsed–laser deposition method. The growth chamber had been pumped to \( 5.0 \times 10^{-7} \) Torr initially. A Nd–YAG pulsed (10 Hz) laser operating at 266 nm using the forth harmonics was used as a power source for ablation of Si–Fe (95/5 wt%) alloy target [14]. The laser pulse with 98 mJ power focused spot diameter is below 1 mm. The plasma plume was created by illuminating the focused laser pulse onto the target at an angle of 55° with normal direction of the target. The target had set rotating speed to 2 rpm and the target–to–substrate distance was 6 cm. The substrates had been cleaned with chemical solutions that are acetone, methanol and distilled water during 5 min in an ultrasonic cleaner, respectively. Before the growth process was started, the substrate was heated at 700°C for 10 min in the vacuum state. The film was grown immediately after the pre–ablating of target. The nitrogen gas pressure was \( 10^{-3} \) Torr and the temperature condition of the substrate was chosen to 200°C. To increase the alloy crystallinity, the post–annealing process was done at temperature of 600°C for 10 min under nitrogen gas ambient.

The electrical resistivities were measured in the temperature range from 20 to 300 K, by using the two probe measurement, and the structural properties were observed by x–ray diffraction (XRD), and EDS spectra. The SQUID was used to obtain the magnetic properties of the grown samples from 10 to 350 K. The magnetic field was varied in the range ±3,000 Oe. The ferromagnetic contribution to the magnetization was extracted from the hysteresis loops after substraction of a diamagnetic behavior.

III. Results and Discussions

Fig. 1 shows the XRD pattern or the as–deposited and post–annealed samples of Fe–diluted Si alloy. The pattern for the alloy sample spectrum has a few of peaks with cubic type structures. The indicated main peak indexation corresponds to the cubic Si (004) phase. The crystal orientation of Fe–diluted Si

![Figure 1. X-ray diffractogram for an as–prepared sample and a post–annealing sample. Here, the \( \theta \)-2\( \theta \) scans shows a peak of FeSi alloy structure at lower angle side of (004) Si substrate diffraction.](image-url)
alloy grows along to the Si (004) substrate during thermal annealing process. The peaks of 61.314, 65.500, and 66.046 degrees can be regarded as FeSi, Fe2Si, and Fe5Si3 alloys [15]. It is evident that our samples are locally showed the forms of the alloy structures because x-ray is more sensitive to large crystallites such as Si substrate.

Fig. 2(a) and (b) show cross-sectional FE-SEM image and EDS spectrum of Fe-diluted Si alloy grown with post annealing at temperature of 600°C, respectively. Here, Fig. 2(a) is a typical cross-sectional FE-SEM micrograph, which was obtained by condition of 15.0 kV, 8.0 mm working distance and at magnification of 200 K, The layer thickness was 90 nm with growth rate of 1.5 nm/s. The chemical compositions of the Fe-diluted Si alloy were measured by EDS as shown in Fig. 2(b). The peaks of Si, O and Fe elements are presented in the EDS spectrum with processing option of all elements analyzed (normalized). The atomic percent of Fe was composed about 1.25∼6.49% (or weight percent of 1.54∼6.67%), which corresponds to the Fe-diluted Si alloy region.

Fig. 3 shows the resistivity of alloy film as a function of the reciprocal temperature. The substrate contribution to the conduction becomes dominant in the region with the temperature between 320 and 90 K, which behaves like an extrinsic semiconductor with the activation energy of $E_{a1}$. At the temperature less than 60 K, the carriers of $p$-type Si substrate becomes freeze-out and the resistivity increase exponentially with activation energy of $E_{a2}$. Many defects may be induced in Fe-diluted Si alloy structure due to the incorporation of Fe atoms. The lattice distortion arises from the mismatch in lattice constant, one should be aware that the expansion coefficients might be different at other temperatures. The resistivity shows an exponential increase with the reciprocal temperature, with activation energy of $E_{a1}=7.79$ meV and $E_{a2}=5.21$ meV, respectively. This anomalous behavior in the vicinity of the transition on resistivity according to temperature is not taken into account fully in the analytical expression. It occurs that a Fermi level for a $p$-type semiconductor moves

![Figure 3](image-url)

**Figure 3.** Resistivity of the alloy sample without post-annealing as a function of the reciprocal temperature.
closer to the valence band as the temperature decrease, It may affect to magnetic properties due to the change of the activation energy. Therefore, the resistivity property of the alloys shows that cannot be revealed due to distribution of local areas of the Fe–diluted Si alloy. And we expected to be various phenomena on Hall resistivity and mobility from pure p-type Si substrates of doped-transition metal such as Fe and Mn. However, our experiments are consistent with the results due to the contribution to alloy structure with Fe atoms (the data does not appear in the paper).

The magnetization versus temperature (M–T) curves for the samples with and without post-annealing measured by SQUID is shown in Fig. 4(a). The measurements of M–T curves are executed by the field cooling procedures on an applied of 3,000 Oe. Despite of the distribution in local area with Fe–diluted Si alloy, the magnetization is affected by sum of local magnetic moment. The value of magnetization is slowly decreasing as increasing temperature, which influenced that magnitude of applied magnetic field is larger than saturation magnetic field as well as coupling of magnetic ions. The maximum value of the magnetization is about 100 emu/cc at the temperature of 10 K, And the ferromagnetism is also appeared until the temperature of 350 K. Fig. 4(b) showed the magnetization versus an applied magnetic field (M–H) curves at the temperature of 10 K for the samples with and without post-annealing. The ferromagnetic hysteresis loops are observed in the Fe–diluted Si alloy after subtraction of the linear diamagnetic background from the p-type Si substrates. Low hysteresis loop such as soft magnetic materials appears at the post-annealed sample. The magnetization depends on the applied magnetic field and temperature. From experimental point, it is very difficulty to avoid the clustering and alloying of impurities during preparation processes of diluted system, This is a reason why the magnetic properties of diluted magnetic semiconductor systems are very sensitive to sample preparation and annealing processes.

IV. Conclusion

The Fe–diluted Si alloys were grown on p-type Si (100) substrates by pulsed–laser deposition with Si–Fe (95/5 wt%) alloy target. The formation of alloy structures such as FeSi, Fe₃Si, and Fe₅Si₃ were characterized by XRD. It was also confirmed that the concentration of Fe atom in alloy film appears in the range of about 1.25 ~ 6.49 atm %. There was the activation energy of 5.21 and 7.79 meV from the re-
sistivity as a function of the reciprocal temperature. The maximum value of the magnetization was about 100 emu/cc at temperature of 10 K. The ferromagnetism with applied magnetic field of 3,000 Oe was also indicated until the temperature of 350 K. These results showed that Fe-diluted Si alloy systems have a chance to applications of spintronic device.

Acknowledgments

This work was supported in part by the National Research Foundation of Korea (NRF) grant funded by the Korea Government (MEST) (Nos. 2011–0027514, 2012–0003067, and 2012–0005053).

References

펄스레이저 증착법에 의한 Fe 희석된 Si 합금의 구조 및 자기 물성 연구

서주영・이경수・박상우・김은규*

한양대학교 물리학과, 서울 133-791

(2012년 7월 10일 받음, 2012년 9월 21일 수정, 2012년 9월 24일 확정)

펄스레이저 증착법으로 P형 실리콘(100) 기판위에 증착한 Fe 희석된 Si 합금의 구조와 전기적 및 자기적 물성을 연구하였다. 합금시료에 대한 X-선 회절패턴에서 육방정계에 해당하는 FeSi, Fe3Si, 및 Fe5Si3와 관련된 여러 개의 회절신호가 관측되었으며, 에너지분산분광 측정에 의한 시료내 Fe 원자의 함량은 1.25 ~ 6.49 at%, %로 나타났다. 또한, 온도변화에 따른 전기비저항 값의 측정으로부터 5.21 meV와 7.79 meV 두 개의 활성화에너지를 얻을 수 있었다. 절대온도 10 K에서 측정한 최대 자화 는 약 100 emu/cc로 나타났으며, 3,000 Oe의 외부자기장하에서 온도의 함수로 측정한 자화 값으로부터 시료의 강자성 특성 은 350 K까지도 유지됨을 알 수 있었다.

주제어 : Fe 희석된 Si, 강자성, 펄스레이저 증착법, 희박자성반도체

* [전자우편] ek-kim@hanyang.ac.kr