AN ABNORMAL BEHAVIOR OF NANO-CRYSTALLINE IN SiO_2 SUBSTRATE

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ABSTRACT

Temperature dependence of the hyperfine field of Fe nanocrystalline in SiO_2 matrix prepared by using an ion implantation and subsequent heat treatment can not be described by a formula for the isolated Fe nanocrystalline. The large stresses or chemical bond force to which interface atoms may be subjected lead to increase effective anisotropic constant. In addition a little concentration of oxygen atoms contained in the crystalline might enhance the hyperfine field.

Keywords Mossbauer spectroscopy, Ion implantation, ^{57}Fe nano-crystalline, SiO_2 substrate

1 INTRODUCTION

The magnetic properties of microcrystals are currently a subject of considerable interest. In many studies of small particles it has been found that the magnetic hyperfine splitting below the supermagnetic blocking temperature is smaller than that found in larger crystals[1,2]. This effect has been explained by oscillations of magnetization around an minimum energy by M ϕrup and Tops ϕe.[3] They derived a formula which describes the hyperfine fields related to the particle volume as follows. $H(V, T) = H(V=\infty, T)(1-KT/2KV)$, where KT is the thermal energy and K is related to the anisotropic constant. The hyperfine (hf) field changing with temperature follows this formula for the isolated particles[3]. However the hf field somewhat deviates from it for the nano-crystalline materials made by compacting under high-vacuum[4].

Recently we prepared ^{57}Fe nano-crystalline in SiO_2 by ion implantation[5]. The hf fields with temperature from room temperature (RT) to 80K were measured by Mossbauer spectroscopy. The results show the hyperfine field values of the α-Fe granules are larger than that of the bulk α-Fe at corresponding temperatures, especially at 80K by 1.3 %. In addition, the magnetic coercivity H_c which is two

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orders of magnitude higher than bulk Fe was measured for this Fe granules.

2 EXPERIMENTAL

Nano-crystalline was prepared by ^{57}Fe ion implantation on SiO_2 and subsequent isochronal annealing in hydrogen atmosphere with a pressure of 4×10^4 Pa for 30 min from 300 to 700 °C. The dose and energy of the Fe ions implanted were 5×10^{16}at / cm^2 and 60 keV, respectively. The beam current implanted in an area with a diameter of 10 mm on the SiO_2 was about 0.3 μA. The location and the state of Fe ions as implanted and annealed in SiO_2 were monitored by using conventional Mossbauer spectroscopy with a source of ^{57}Co in Pd. The sample subjected to annealing at 650°C for 30 min was measured by Mossbauer spectroscopy from RT to 80 K in order to investigate the temperature dependence of the magnetic hyperfine field. A parallel measurement was also performed on α-Fe foil for comparison.

The magnetic properties were measured by using a vibrating sample magnetometer (VSM) with an external field range of 0—16 / 4π MA / m at room temperature and liquid nitrogen temperature, respectively. The size of the Fe granules was determined by transmission electron microscopy (TEM).

3 RESULTS AND DISCUSSION

The Mossbauer spectra taken from RT to 80 K are shown in Fig.1 for the sample after annealing at 650°C for 30 min. The size of Fe granules observed is about 25 nm. The spectra clearly shown that the magnetic Fe indicated in a sextet in the spectra is formed besides the paramagnetic Fe during annealing process. It means the precipitation of the iron atoms in SiO_2 matrix took place at high temperature because only the paramagnetic components appeared in Mossbauer spectra for the as implanted sample[5]. However it is not surprising due to the fact that Fe and SiO_2 are thought to be insoluble.

Table 1

Mossbauer parameters of nanocrystalline Fe at 80K

	H / keV	δ / mm · s^{-1}	Γ / mm · s^{-1}	A / %
Fe crystal	343	0.17	0.24	41
Interface	316	0.20	0.63	17

H: hyperfine field, δ: isomer shift, Γ: full line width, *A*: relative area

In contrast to the sharp lines of the sepctrum of an α-Fe calibration foil, the magnetic component of the nanocrystalline in SiO_2 are strongly and asymmetrically broaden. It can be decomposed into two components: a sharp one and a broad one. According to the structural considerations, they correspond to the crystalline and the interfacial atoms respectively. The spectra were fitted by a least square fitting program. The isomer shift (IS) values reported in this work are relative to α-Fe foil. Hyperfine parameters and intensities at 80 K for

magnetic components are summarized in Table 1.

The crystalline component shows a larger hyperfine field, whereas a smaller field for the interfacial component. In addition, in the middle of the Mossbauer spectra it can be resolved into three paramagnetic components along with the contributions from the third and fourth lines of magnetic sextets. Their contributions are a single line (S) and two quadruple doublets (D_1, D_2) as shown in Fig.1. The singlet could

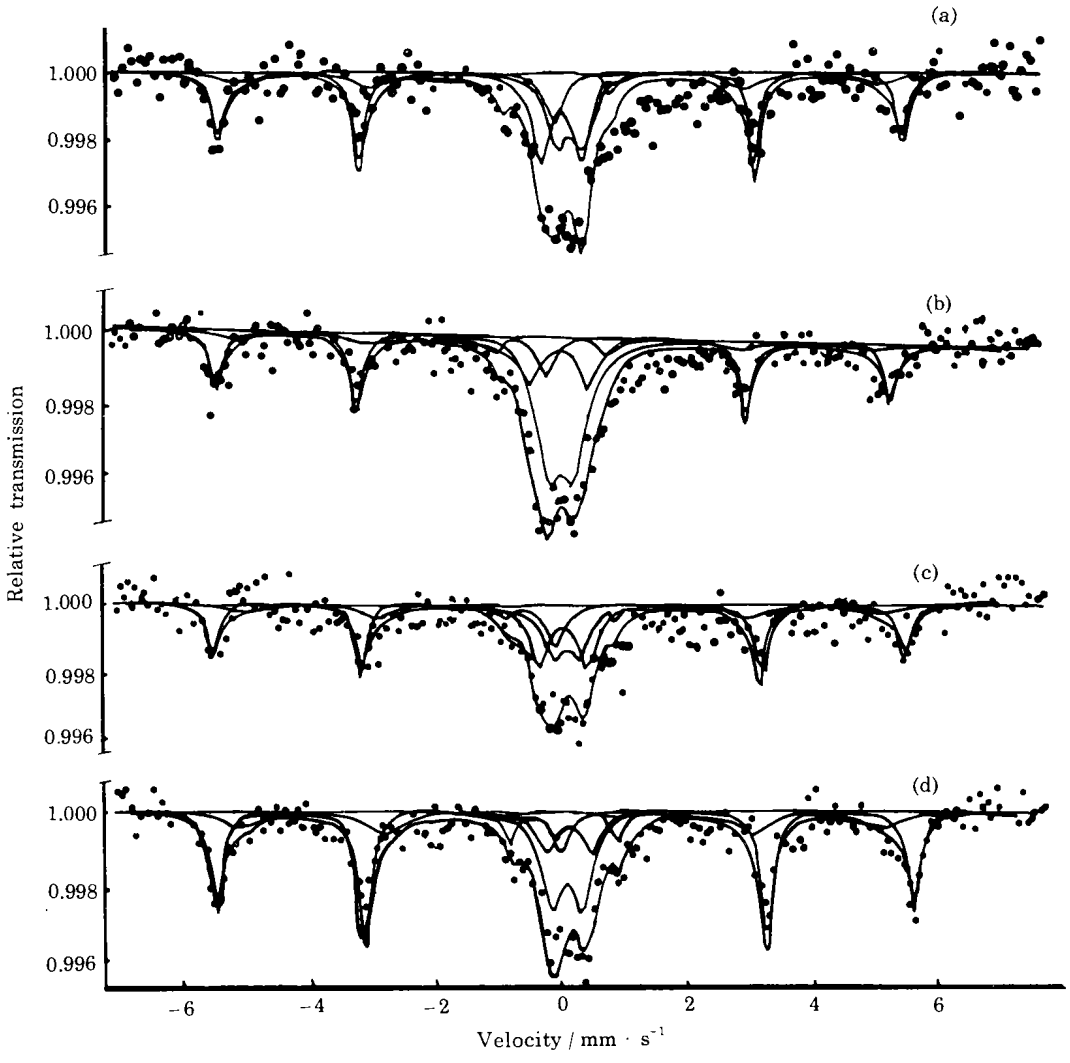

Fig.1 Mossbauer spectra as a function of measuring temperature

(a) RT (b) 173 K (c) 123 K (d) 80 K

probably be attributed to a small cluster of matallic Fe with superparamagnetic behavior dispersed in the SiO_2 matrix. Other two doublets (D_1, D_2) could be attributed

to Fe^{2+} and Fe^{3+} states, respectively, in Fe–Si–O type complexes, forming smaller clusters[6]. This explanation is supported by the fact that their intensities relative to sextets from larger size of Fe nanocrystalline reduced strongly with a decrease of temperatures.

The hf fields as a function of measuring temperature for both Fe nanocrystalline and Fe foil are presented in Fig.2. The relations between the hyperfine field and temperature as shown is close to linear. However the hyperfine field values of nanocrystalline are somewhat higher than that of bulk α–Fe in the temperature region from RT to 80 K, particularly in lower temperature side. It means the temperature dependence of hyperfine field of Fe nanocrystalline in SiO_2 matrix can not be described by the formula derived by M ϕrup and Tops ϕe for the isolated Fe nanocrystalline. In Fe–SiO_2 system, the Fe atoms in the interface of crystalline probably bond with the insoluble matrix forming a structure without long or short range order. These interface atoms may be subjected to large stresses or chemical bond force which lead to increase effective anisotropic constant (K) which is normally related to H_c and probably also lead to influence the thermal oscillations of the magnetization as a single domain. At room temperature, a coercivity H_c of $100/4\pi$ kA/m which is two orders of magnitude larger than that of bulk Fe was observed by VSM. At liquid nitrogen temperature, a little smaller value of H_c was observed[5]. In addition, the strongly bonded oxygen–rich iron compounds, as is known, have a higher field value than for α–Fe[6]. Therefore it can not be excluded that a little concentration of oxygen atoms contained in the crystalline enhance the hyperfine field.

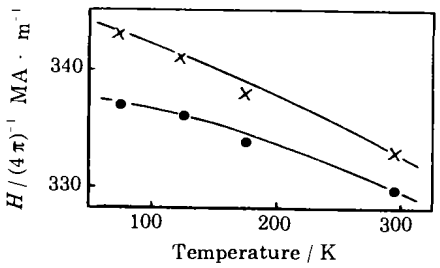

Fig.2 Temperature dependence of the magnetic hyperfine field of Fe

Cross symbols: nanocrystalline compont

Solid symbols: α–Fe foil

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