Thermodynamic behavior of ^{57}Fe implanted into $ZrO_2(Y)$ by CEMS and slow positron beam*

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Abstract Using conversion electron Mössbauer spectroscopy(CEMS) and slow positron beam, the chemical state of ^{57}Fe (100 keV, 3 $\times 10^{16}$ cm^{-2}) implanted into ZrO_2 containing 0.03 mole fraction Y_2O_3 (ZY_3) and its thermodynamic behavior during annealing process at 200 ~ 500°C are studied. For as-implanted sample, Fe chemical states of Fe^0, Fe^{2+} and Fe^{3+} are observed, and assigned to the superparamagnetic metallic iron cluster, iron dimer (and trimer) and complex of the Fe^{3+} associated with cation vacancy (V) and oxygen, respectively. After annealing at 400°C the complexes of Fe^{3+}-V are mostly dissolved, and the prior phase to α-Fe and α-Fe nano- crystalline cluster are present in the sample. Meanwhile the mixed conducting of oxygen-ions and electrons in the ZY_3 sample containing Fe appears, it may correlate with the different iron charge states and their relative amounts, in particular with the α-Fe nano-granule.
Keywords ^{57}Fe ion beam, α-Fe, Nano-granule, Conversion electron Mössbauer spectroscopy, Positron annihilation Doppler broadening spectra

1 Introduction

The solid solution of ZrO_2 with Y_2O_3 is a good oxygen ion conducting electrolyte[1,2] at elevated temperature. Electron-ion mixing electrode could be formed on the surface layer in the $ZrO_2(Y)$ by Fe ion implantation, they help a very thin layer without sharp interface form between the top layer and the ZY_3 specimen and save electrical power. The properties of the implanted material depend on the micro structure connecting with thermodynamic behavior of the implanted ions. Burggraaf *et al* [2] and Marest *et al* [3] studied thermodynamic process of the implanted iron in ZrO_2 and ZY_3 in vacuum and in argon atmosphere, respectively. But the RBS results were evidently different. Marest *et al* [3] found that Fe depth profile for the annealed sample at 500°C was obviously different from that for as-implanted. But Burggraaf *et al* [2] found that Fe depth profile did not change for the annealed sample, even after annealing at 900°C. However, they both found that fine cluster Fe_2O_3 was formed after annealing at 400°C. In order to keep the implanted Fe ions in low vacuum from oxidation during annealing process, we annealed samples in hydrogen atmosphere. Using CEMS and Doppler broadening spectra of slow positron annihilation radiation, we have studied the valence states and structural configurations for the as- implanted Fe ion, and their aggregation with annealing temperatures, obtaining the relationship between Fe nano-meter clusters and the electron conducting for the samples under study.

2 Experimental procedures

2.1 Samples

The samples of ZY_3 were formed by mixing Y_2O_3 (0.03 mole fraction) powder and ZrO_2 powder homogeneously and pressing into a cake with a diameter of 20 mm, then sintering at 1600°C for 3 h and tempering at 500°C for 1 h. ZY_3 samples were implanted with $^{57}Fe^+$ beam (100 keV) at room temperature in 1.33×10^{-4}Pa and its fluence is $3\times10^{16}cm^{-2}$, corresponding

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atom fraction is ~0.06, the implanted area is about 1 cm^2. Finally, the isochronal thermal treatment was performed in hydrogen in sequence from 200 to 500°C for 30 min.

2.2 CEMS measurement

Mössbauer spectra were taken in back scattering geometry, measuring the conversion electron by resonant counter with 0.05 volume fraction CH_4 in helium gas flow electron counter at room temperature. Mössbauer source is ^{57}Co(Pd) with 555 MBq. The isomer shift (IS) is relative to a metal iron.

2.3 Slow positron annihilation

The experiments were performed using a variable-energy positron beam of USTC[4]. The samples were mounted on the top of the bar with high voltages in the high vacuum (0.133 mPa) target chamber. The FWHM of energy dispersion of slow positron was less than 2 eV, the energy could vary between 0~18 keV. The positron annihilation Doppler broadening spectra were measured by the intrinsic high pure Ge detector as a function of the positron energy(E) from 0.5 to 18keV. The data were analyzed in terms of the S parameter, which is the ratio of γ-ray counts at the central part of the 0.511MeV annihilation peak to the total counts contained in the whole peak.

3 Experimental results

3.1 CEMS of Fe in the as-implanted samples

Fig.1a presents CEMS spectra measured at room temperature of ZY_3 sample implanted with ^{57}Fe of 100 keV and with a dose of 3×10^{16} cm^{-2}. The Mössbauer parameters are shown in Table 1, which is obtained from fitting spectra with the least square procedure with the assumption of Lorentzian shape of Mössbauer lines. From the consistent fit, CEMS spectrum in Fig.1a can be decomposed to four quadrupole-split doublets and one singlet. The later can be ascribed to superparamagnetic metallic α-Fe, due to its IS closes to zero. This viewpoint is consistent with those of Burggaaf[2] and Marest[3]. It can be found that the relative intensity (RI) of sextet for α-Fe with ion energy of 15 keV and dose of 8×10^{16} cm^{-2} by Burggraaf *et al* is stronger than that obtained by Marest *et al* with ion energy of 100 keV and fluence of 8×10^{16} cm^{-2}. For our sample the concentration of Fe in ZY_3 is smaller than those of their samples. Therefore, the probability of forming metallic iron (α-Fe) grain with large size should be much smaller, i.e. the superparamagnetic peak maybe belongs to small iron clusters.

Table 1 IS, QS, W(line width), H_f and RI as a function of annealing temperatures for the ZrO_2 implanted with ^{57}Fe

		As-impl	200°C	400°C	500°C
I	IS/mm·s^{-1}	-0.01	-0.02	-0.01	-0.01
	W/mm·s^{-1}	0.38	0.45	0.50	0.46
	RI	0.06	0.07	0.06	0.02
II	IS/mm·s^{-1}	0.20	0.21	0.19	0.19
	QS/mm·s^{-1}	0.73	0.68	0.48	0.82
	W/mm·s^{-1}	0.52	0.52	0.58	0.68
	RI	0.35	0.33	0.18	0.13
III	IS/mm·s^{-1}	0.30	0.32	0.22	0.48
	QS/mm·s^{-1}	0.93	0.73	0.95	0.96
	W/mm·s^{-1}	0.75	0.74	0.42	0.51
	RI	0.34	0.37	0.13	0.11
IV	IS/mm·s^{-1}	0.86	0.84	0.84	0.84
	QS/mm·s^{-1}	0.77	0.77	0.77	0.77
	W/mm·s^{-1}	0.67	0.66	0.66	0.66
	RI	0.06	0.07	0.11	0.04
V	IS/mm·s^{-1}	1.12	1.07	1.07	1.04
	QS/mm·s^{-1}	2.12	2.29	1.94	1.91
	W/mm·s^{-1}	1.06	0.85	0.51	0.92
	RI	0.18	0.15	0.12	0.16
VI	IS/mm·s^{-1}	–	–	0.24	0.25
	QS/mm·s^{-1}	–	–	0.02	0.03
	H_f/kOe	–	–	199.3	208.4
	W/mm·s^{-1}	–	·	0.83	0.48
	RI	–	–	0.40	0.23
VII	IS/mm·s^{-1}	–	–	–	0.04
	QS/mm·s^{-1}	–	–	–	0.001
	H_f/kOe	–	–	–	328.7
	W/mm·s^{-1}	–	–	–	0.27
	RI	–	–	–	0.30

Four doublet components in the spectrum are divided to two groups. One is IS=0.2~0.3 mm/s and QS=0.7~0.9 mm/s. The other is IS= 0.85~1.12 mm/s and QS=0.70~2.10 mm/s. These hyperfine parameters correspond to the typical high spin states of Fe^{3+} and Fe^{2+}, respectively. Comparing the experimental results with the binomial distribution of the implanted ions, it is found that some of iron ions implanted into ZrO_2[5], Al_2O_3[6] and MgO_2[7] exist in the isolated ion state with IS=0.24~0.4 mm/s and QS=0.4~1.0 mm/s. These isolated Fe^{3+} ions are probably combined with the cation vacancies(V) and O^{2-} ions to form the complexes.

Shell - model calculations[8] of the stability

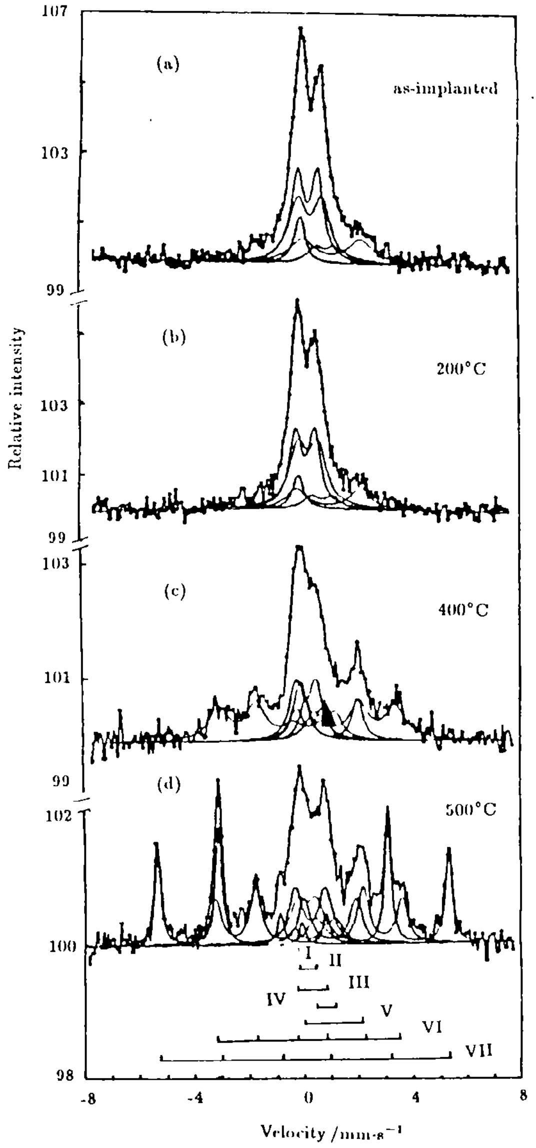

Fig.1 CEMS for $ZrO_2(Y)$ implanted with ^{57}Fe
I–Fe^0, II–Fe_I^{3+}, III–Fe_{II}^{3+}, IV–Fe_I^{2+}, V–Fe_{II}^{2+}, VI–Prior phase to α–Fe VII–α–Fe

energy of various Fe^{3+}-vacancy complexes indicated that Fe^{3+}–O^{2-}–V–O^{2-}–Fe^{3+} trimer is the stablest configuration. It is also found that the local states of ^{57}Fe in substrate were determined by electric neutral metal -vacancy configuration[5], such as Fe^{3+}–O^{2-}–V or V–O–Fe^{2+}–O–V complexes. Therefore, it is not clear yet for the Fe^{3+} configuration in the ZY_3 samples. Maybe, several different configurations of Fe-O-V exist because two groups of Mössbauer parameters were found in this study. As it is well known that many oxygen vacancies(V_o) in ZrO_2 are formed by Y mixed in ZrO_2, e.g. $Y_2O_3 \rightarrow 2Y_{Zr}^{3+}+Vo+3O^{2-}$. Therefore they must influence the configurations of Fe^{3+} ions. We assume that Fe_{II}^{3+} with larger IS is combined with more vacancies and less O^{2-} ions, compared to Fe_I^{3+} with smaller IS. We also can not exclude the possibility that Fe_{II}^{3+} may be Fe^{4+}ion which located in distorted FeO_6 octahedral site, as isomer shift of Fe_I^{3+} is a little smaller than that of the typical isolated Fe^{3+} ions.

It is found that Fe ions implanted into $ZrO_2^{[5]}$, $Al_2O_3^{[6]}$ and $MgO_2^{[7]}$ can formed two different Fe^{2+} ion sites, Fe_I^{2+} and Fe_{II}^{2}, where Fe_I^{2+} represents iron in dimer, Fe_{II}^{2+} in trimer and other more complicated configurations. The IS and QS values for these components are close to the values in Table 1. So we presume that the doublet with IS = 1.12 and QS = 2.1 mm/s is attributed to Fe_{II}^{2+} and the doublet with IS = 0.86 and QS =0.77 to Fe_I^{2+}.

3.2 Thermodynamic behavior of Fe implanted into ZY_3

After annealing at 200°C , RI for each component is nearly the same as that for as-implanted state (see Fig.2). Upon annealing at 400°C RI for Fe^{3+} decreased from 0.70 of the as-implanted to 0.30, in which RI of Fe_I^{3+} and Fe_{II}^{3+} decreased from 0.41 to 0.18 and from 0.29 to 0.125, respectively. Meanwhile a ferromagnetic phase prior to α-Fe phase appeared[9], it has a small hyperfine field, H_f=199.3 kOe. These results show that Fe^{3+}-O-V complexes began to decompose, a part of Fe^{3+} ions was reduced to Fe^0, then these atoms were gathered into small clusters by the interaction among Fe^0 atoms.

After annealing at 400°C, about 0.40 of Fe^{3+} ions are reduced to Fe^0, but the relative amount of the Fe^{2+} component was nearly unchanged, it is probably as a result of competition between forming Fe^{2+} dimer or trimer from decomposed Fe^{3+} and transforming them to α-Fe. Annealed up to 500°C, a ferromagnetic phase with sextet appeared in the Mössbauer spectrum, H_f=329 kOe and IS=0.04 mm/s close to those of metallic Fe. Therefore, this magnetic component should be assigned to α-Fe. Meanwhile, the intensities of the superparamagnetic component and the magnetic component with small hyperfine field were reduced significantly. This result indicates that α-Fe phase was transformed from them. In addition, Fe^{3+} ions may be a complexes associated with vacancy and oxygen ion O^{2-} only with different configurations, because the annealing behaviors for both Fe_I^{3+} and Fe_{II}^{3+} are similar to each other.

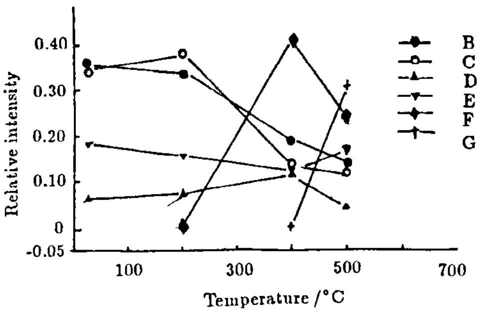

Fig.2 RI of various components as a function of annealing temperatures

B–Fe_I^{3+}, C–Fe_{II}^{3+}, D–Fe_I^{2+}, E–Fe_{II}^{2+}, F–Prior phase to α–Fe, G–α-Fe

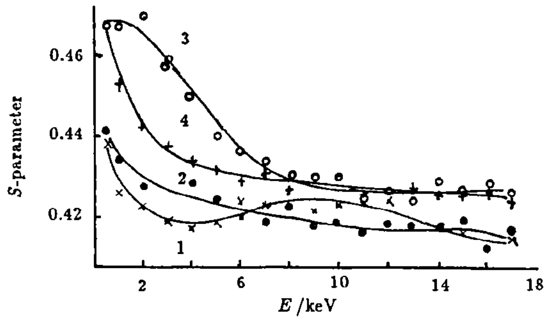

Fig.3 Doppler parameters $S-E$ curves measured by slow positron beam

1. ZY_3 unannealed 2. ZY_3 annealed at 500°C 3. As-implanted ^{57}Fe in ZY_3 4. Annealed at 500°C for ^{57}Fe implanted ZY_3

3.3 Slow positron beam studies

Curve 1 in Fig.3 shows that S parameter for positron energy of 2~5 keV (corresponding to 20~90 nm in depth) is smaller than that for positron energy of 6~12 keV (corresponding to 120~360 nm in depth). It means that there exist more positron trapped centers in the inner layer than those on surface during sintering process of $ZrO_3(Y)$ samples. It can be attributed to Y element enriching, bringing about more un- intrinsic cationic vacancy[10,11] (trapped center) in the deeper region. For the curve 3 in Fig.3 there is a sharp increase in S parameter in 0.5~6 keV (2.2 ~ 120 nm). It indicated that ^{57}Fe implantation produced a large amount of cationic vacancies, then the Fe^{3+}-O^{2-}-V complexes were formed. This result strongly supports the CEMS result mentioned in section 3.1. According to calculation by Trim program, the deepest depth for implanted ^{57}Fe with 100 keV is about 40 nm underneath the surface, this value consists with the depth where the largest S-parameter was obtained from slow positron beam. Therefore the larger S-parameter indicates the more vacancy density produced by ion collision. The curve of $\Delta S_{3-1}(= S_3 - S_1)$ presents the difference between the iron implanted ZY_3 and ZY_3 substrate. From the curve the positron trapped center profile produced by iron implantation is able to be obtained. The trapping centres in the outer layer approach to the results calculated by Trim program, but ΔS in the inner (120 ~ 632 nm) is smaller due to lower concentration of Fe ions. It is also evident from the curve that vacancy density produced by ion collision is much higher than the un-intrinsic cation vacancy produced by Y doping. After annealing at 500°C, the difference between the $S-E$ curve 2 for substrate ZY_3 and the $S-E$ curve 4 for ^{57}Fe ion implanted ZY_3 are rather small. It means that after annealing oxygen desorption on the surface of ZY_3 and/or homogenizing of the micro structure of ZY_3 took place for the substrate ZY_3, and the ion irradiation defects were recovered for the implantation sample and the trapping centers decreased. The difference between curves 2 and 4 is nearly constant, ΔS_{4-2}=0.0012. The difference shows that there still exists a certain amount of Fe^{3+}-O-V complexes in the specimen after annealing at 500°C. This result is consistent with that of CEMS. The remained complexes probably need higher temperature for dissociation.

4 Discussion

For iron implanted ZrO_2, Al_2O_3 and MgO samples, it was found that under different annealing conditions the results could be quite different[5,6,7], especially for annealing in vacuum and in air. As well known, iron atom is an element to be easily oxidized, even at depth of ~50nm by implantation with energy of 100 keV. Some of oxygen atoms can diffuse into the crystalline through crystal boundary or vacancies, oxidizing Fe^{2+} to Fe^{3+} that is so called internal oxidation.[12,13] For our sample ZY_3, all Fe^{2+} ions were oxidized into Fe^{3+} at 550°C in the mixture atmosphere of 2.66 kPa hydrogen and 1.33 kPa air . Therefore, high vacuum or hydrogen protection measures must be adopted in studying thermodynamic behavior of Fe ions implanted into sample.

Solid solution ZY_x is an excellent oxygen ion conducting electrolyte with high strenth when the doped Y produces oxygen vacancy, and oxygen ions migrate between the vacancies. After doping Fe element into ZY_3, the ZY_3 could become mixed conducting electrolyte.[14,15] The electron conducting is caused by electron transition between the electron charge states of Fe ions. For Fe doped ZY_3 sample the electrical conductivity experiment[16] shows that the electrical conductivity at 300°C is $3\times10^{-6}\Omega^{-1}cm^{-1}$, it is one order of magnitude higher than that for the Fe undoped samples. Therefore we suppose that the larger conductivity might connect with α-Fe cluster of small size formed during annealing. After forming a certain amount of Fe, electron conducting is induced by the transfer of charges among Fe^0, Fe^{3+} and Fe^{2+}.

5 Conclusion

From the results of CEMS, Fe ions implanted into ZY_3 sample exist in Fe^{3+}, Fe^{2+} and Fe^0 states. Fe^0 resides in the form of cluster with superparamagnetic behavior. The Fe^{2+} ions are formed iron dimer and trimer. The Fe^{3+} ion is ascribed to the isolated Fe ion located in the environment without iron near neighbourhood, but associated with cationic vacancy and oxygen and formed Fe^{3+}-V or Fe^{3+}-O^{2-}-V complexes in ZY_3. Upon annealing at 400°C and 500°C, Fe valence states changed, meanwhile the Fe^{3+}-O^{2-}-V complexes were decomposed, vacancies disappeared mostly, and Fe configuration changed. Under the annealing condition with dilute hydrogen α-Fe with large size (> 5nm) was formed due to preventing from Fe oxidation. $S-E$ curves fully prove that a large amount of cationic vacancies were induced by Fe ion implantation, and their distribution corresponding to the implantation zone. After annealing at 500°C, $S-E$ curve shows that those vacancies disappeared mostly. So it provides a new evidence for assigning sites of Fe in ZY_3. At 300°C mixed conducting appeared in ZY_3 sample. It probably correlates with different iron charge states, especially with amount of Fe^0 compared with those of Fe^{2+} and Fe^{3+}.

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