copper deposits appear very clearly on the scratched SiO_2 location, such as in Fig. 7.

However, the wafer handled with a well designed carrier is scratched shallower, and even by copper decoration method, it is difficult to clarify the origin of copper decoration dot one by one, in order to measure pinhole density normally engendered.

This is the reason why the number of decorations located in the peripheral regions on the examined wafers were not counted to determine the relation between the pinhole densities and the SiO_2 thickness, as explained in 3.3.

4 Conclusion

An optimum CuSO_4 concentration for copper decoration at 40°C was 0.01 M under the applied voltage which is derived as a multiplication of the SiO_2 thickness and 2.5×10^6 V/cm. Under these conditions, the relationship between the pinhole densities and the film thickness was examined, and it was found that the relationship between SiO_2 thickness and pinhole density coincides with that obtained by aluminum anodization method. Copper decoration method is indicated as being a convenient method to

investigate the origin of pinholes, such as mis-handling of a Si wafer.

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Formation of $\epsilon\text{-Fe}_2\text{O}_3$ in the Vapor Phase Oxidation of Iron (II) Chloride

Akio KATO* and Shigeki MATUYA*

The vapor phase oxidation of iron (II) chloride at 700°C to $1,000^\circ\text{C}$ was found to give $\epsilon\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ as the main products and $\gamma\text{-Fe}_2\text{O}_3$ as the minor one, in contrast to the oxygenolysis of iron (III) chloride which gives $\eta\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ under similar reaction conditions. The formation process of Fe_2O_3 particles is discussed.

1 Introduction

Besides the well-known modifications of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$, the presence of $\epsilon\text{-Fe}_2\text{O}_3$ has been reported by several investigators^{1)~3)}. In 1934, Foreister *et al.* found the formation of magnetic diiron trioxide by the thermal decomposition of $\text{Fe}_2\text{O}_3 \cdot 4\text{BeO}$ ¹⁾. In 1963, Schrader *et al.* found a new diiron trioxide phase, different from $\alpha\text{-Fe}_2\text{O}_3$

and $\gamma\text{-Fe}_2\text{O}_3$, by electric d-c arc discharge between iron electrodes under oxidizing atmosphere and named it $\epsilon\text{-Fe}_2\text{O}_3$ ²⁾. Later, Trautmann *et al.* showed that the above two diiron trioxides were identical and found a new preparation method of $\epsilon\text{-Fe}_2\text{O}_3$ ³⁾. In addition, the formation of another modification, $\eta\text{-Fe}_2\text{O}_3$, by vapor phase oxygenolysis of iron (III) chloride has recently been reported⁴⁾.

The present authors found that three kinds of diiron trioxides, $\epsilon\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ were pro-

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duced by the vapor phase oxidation of iron(II) chloride. In this study, the effects of reaction conditions on the formation ratios of these three diiron trioxides were investigated. The results were compared with those of the oxygenolysis of iron (III) chloride.

2 Experimental

The reaction was carried out by a flow method. The apparatus is shown in Fig. 1. A silica glass tube was used as the reactor. The furnace consists of two parts, one part (I) for the evaporation of iron chloride and the other (II) for reaction. Anhydrous iron (II) chloride was obtained by the dehydration of $\text{FeCl}_2 \cdot n\text{H}_2\text{O}$ (Wako Junyaku Kogyo, G.R.) at about 250°C in dried N_2 . In the vapor phase oxygenolysis of iron (III) chloride, anhydrous FeCl_3 (Ishizu Seiyaku, G.R.) was used without further purification.

FeCl_2 (7–8 g) was evaporated in a mullite boat at 750°–900°C and carried into the reaction zone by deoxygenated and dried N_2 , being mixed with O_2 . In the oxygenolysis of FeCl_3 , FeCl_3 (7–8 g) was evaporated in pyrex boat at 250°–260°C. The reaction temperature was between 700° and 1000°C. Diiron trioxide powders produced were collected with a 1 l flask. The concentrations of iron chlorides in the gas phase were controlled by the evaporation temperatures and determined from the amount of freed Cl_2 measured by iodometry. Identification of each diiron trioxide phase in the products was done by X-ray diffraction ($\text{CoK}\alpha$). The amount of each phase in the product of the oxidation of FeCl_2 was

Fig. 1 Apparatus

- 1: Silica glasse tube (30 mm I.D.)
- 2: FeCl_2 or FeCl_3 source
- 3: CA thermocouple
- 4: Collecting flask (1 l), (I): Evaporation zone
(II): Reaction zone

determined from the intensity of the strongest line of each phase ($\epsilon\text{-Fe}_2\text{O}_3$: (420), $\alpha\text{-Fe}_2\text{O}_3$: (104), $\gamma\text{-Fe}_2\text{O}_3$: (311))*¹. The contents of Fe^{3+} and Fe^{2+} in the products were determined by titration with 0.01 M EDTA and 0.05 N KMnO_4 , respectively.

3 Results and Discussion

In the vapor phase oxidation of iron(II) chloride, $\epsilon\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3$ are the main products and $\gamma\text{-Fe}_2\text{O}_3$ is the minor one. On the other hand, in the case of iron (III) chloride, $\eta\text{-}$ and $\alpha\text{-Fe}_2\text{O}_3$ are produced under similar conditions, as reported by Funaki *et al.*⁴. The identifications of reaction products by X-ray diffraction are illustrated in Table 1. The degree of reduction of iron in the products is less than 2% even in the oxidation of FeCl_2 .

Fig. 2 Reaction temperature and phase composition of Fe_2O_3 powders

$[\text{FeCl}_2] = 0.8 \sim 1.4(\%)$, $[\text{O}_2]$; (A) = 40%, (B) = 60%, (C) = 80%, Gas flow rate; 500 ml/min
○: $\epsilon\text{-Fe}_2\text{O}_3$, ●: $\alpha\text{-Fe}_2\text{O}_3$, ◐: $\gamma\text{-Fe}_2\text{O}_3$

*¹ The intensity ratio of the strongest line of each phase was found as; $I_{\alpha\text{-Fe}_2\text{O}_3(104)} : I_{\gamma\text{-Fe}_2\text{O}_3(311)} : I_{\epsilon\text{-Fe}_2\text{O}_3(420)} = 1.00 : 1.33 \pm 0.05 : 1.08 \pm 0.10$. For the overlap of (311) of $\gamma\text{-Fe}_2\text{O}_3$ and (110) of $\alpha\text{-Fe}_2\text{O}_3$, the measured ratio, $I_{\alpha\text{-Fe}_2\text{O}_3(110)} / I_{\alpha\text{-Fe}_2\text{O}_3(104)} = 0.61 \pm 0.03$, was used for the correction. However, there is also a partial overlap between (104) of $\alpha\text{-Fe}_2\text{O}_3$ and (420) of $\epsilon\text{-Fe}_2\text{O}_3$. Then, it seems to be difficult to analyze the mixture of α , γ , and ϵ phases better than 10% accuracy as indicated by Schrader *et al.*²⁾.

Table 1 X-ray diffraction patterns of reaction products

Product A ^{a)}		Reference						Product B ^{b)}		Reference					
		α -Fe ₂ O ₃ ^{c)}		ϵ -Fe ₂ O ₃ ^{d)}		γ -Fe ₂ O ₃ ^{e)}				α -Fe ₂ O ₃ ^{c)}		γ -Fe ₂ O ₃ ^{f)}			
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I		
3.67	20	3.66	25					3.85	20			3.84	20		
3.22	20			3.24	20			3.68	10	3.66	25				
2.97	30			2.98	35			2.71	100	2.69	100	2.72	100		
2.95	5					2.95	34	2.52	25	2.51	50	2.53	10		
2.73	90			2.73	100			2.21	10	2.20	30	2.21	10		
2.70	60	2.69	100					2.00	10			2.00	10		
2.57	10			2.57	8			1.84	20	1.84	40	1.85	10		
2.54	10			2.55	20			1.70	15	1.69	60				
2.52	100	2.51	50			2.52	100	1.66	30			1.66	40		
2.45	30			2.46	30			1.49	10	1.48	35				
2.30	5			2.30	6										
2.24	20			2.24	20										
2.21	20	2.20	30												
2.17	5			2.17	14										
2.09	15					2.08	24								
1.98	10			1.98	20										
1.84	20	1.84	40												
1.73	10			1.74	25										
1.69	30	1.69	60			1.70	12								
1.66	10			1.67	25										
1.61	15					1.61	33								
1.52	25			1.52	35										
1.49	10	1.48	35												
1.47	20					1.48	53								

a) Reaction product of FeCl₂-O₂ system at 900°C,

c) ASTM card 13-534, d) ASTM card 16-653,

b) Reaction product of FeCl₃-O₂ system at 700°C

e) ASTM card 4-0755, f) Ref. 4

3.1 Effects of reaction conditions on the formation ratio of each diiron trioxide phase

Although the determination of the amount of each phases in reaction products accompanies a considerable error^{*2}, one can see the following tendencies between the reaction conditions and the formation ratio of α , γ , and ϵ phases.

The effect of reaction temperature is shown in Fig. 2. The yield of ϵ -Fe₂O₃ shows a maximum and that α -Fe₂O₃ shows a minimum at around 900°C. Figure 3 illustrates the effect of oxygen concentration at 900°C. Similar trends could be seen at 800°C. The effect of oxygen concentration was little at 700°C and 1000°C, except that the yield of γ -Fe₂O₃ increased with

Fig. 3 Oxygen concentration and phase composition of Fe₂O₃ powders

Reaction temperature; 900°C, [FeCl₂]=0.9~1.1 vol% (balance: N₂), Gas flow rate: 500 ml/min. Symbols are the same as in Fig. 2

*2 See *1.

Fig. 4 FeCl_2 concentration and phase composition of Fe_2O_3 powders

Reaction temperature: 900°C , $[\text{O}_2] = 80 \text{ vol}\%$
(balance: N_2), Gas flow rate: 500 ml/min.
Symbols are the same as in Fig. 2

rise in oxygen concentration at 700°C . The effect of FeCl_2 concentration is shown in Fig. 4. The formation of $\gamma\text{-Fe}_2\text{O}_3$ occurs only when FeCl_2 concentration is low. The gas flow rate (300, 500, 900 ml/min) affected little on the yield of three phases.

3.2 Electron microscopic observation

Electron micrographs of the products are given in Fig. 5. The particles have linear edges, suggesting that they are single crystalline. The particle sizes lie between a few thousand Å and 2μ . As seen in Fig. 5 and Table 2, the sizes increase with rise in reaction temperature and FeCl_2 concentration, but vary little with oxygen concentration.

Fig. 5 Electron micrographs of Fe_2O_3 powders (scale; $1\mu\text{m}$) (Reaction condition is given in Table 2)

Table 2 Particle size

Run	Reaction temperature ($^\circ\text{C}$)	Gas composition ^{a)} (balance: N_2)		Mean diameter ^{b)} (μm)
		FeCl_2 (vol %)	O_2 (vol %)	
4	700	1.0	80	0.3
7	800	0.8	80	0.4
8	900	1.0	20	0.7
9	900	1.0	40	0.6
10	900	0.9	60	0.6
11	900	1.1	80	0.7
14	1000	1.0	80	0.6
15	900	1.1	80	0.8
16	900	2.1	80	1.3
17	900	3.7	80	1.6

a) Gas flow rate, 500 ml/min

b) Number-averaged diameter of about 50 particles from 3-4 electron micrographs

3.3 Formation process of diiron trioxide particles

The particle formation in vapor phase reaction consists of two processes; homogeneous nucleation and growth. In the case of vapor phase oxidation of FeCl_2 , a cluster of diiron trioxide, $(\text{Fe}_2\text{O}_3)_n$, is formed and grows into a diiron trioxide particle through the critical nucleus.

The equilibrium constants of the oxidation of FeCl_2 and the related reactions are shown in Fig. 6. The oxidation of FeCl_2 is exothermic and the thermodynamic driving force decreases with rise in temperature. This may be responsible for the increase in particle sizes, that is, the decrease in the nucleation, with rise in reaction temperature.

In the vapor phase oxidation of FeCl_2 , three kinds of phases, ϵ -, γ - and α - Fe_2O_3 are formed. α - Fe_2O_3 is the most stable and the others metastable (Fig. 6). It has been reported that ϵ - and γ - Fe_2O_3 are transformed into α - Fe_2O_3 at about 750°C ^{3), 5)} and at 400°C - 700°C ^{6) ~ 8)}, respectively. In the present study, the reaction product at 800°C (Fig. 2 B) was transformed completely into α - Fe_2O_3 by heating at 550°C for 5 min in air. In the temperature range 700°C - 900°C , however, the yield of ϵ - Fe_2O_3 increases

Fig. 6 Equilibrium constants of related reactions

- 1: $2\text{FeCl}_2(\text{g}) + 3/2\text{O}_2(\text{g}) = \alpha\text{-Fe}_2\text{O}_3(\text{s}) + 2\text{Cl}_2(\text{g})$
 2: $2\text{FeCl}_2(\text{g}) + 3/2\text{O}_2(\text{g}) = \gamma\text{-Fe}_2\text{O}_3(\text{s}) + 2\text{Cl}_2(\text{g})$
 3: $2\text{FeCl}_2(\text{g}) + 3/2\text{O}_2(\text{g}) = \epsilon\text{-Fe}_2\text{O}_3(\text{s}) + 2\text{Cl}_2(\text{g})$
 4: $2\text{FeCl}_3(\text{g}) + 3/2\text{O}_2(\text{g}) = \alpha\text{-Fe}_2\text{O}_3(\text{s}) + 3\text{Cl}_2(\text{g})$
 5: $\text{FeCl}_2(\text{g}) + 1/2\text{Cl}_2(\text{g}) = \text{FeCl}_3(\text{g})$

The heat of formation of $\text{Fe}_2\text{O}_3(\text{s})$, ΔH_{298}° (Kcal/mole) = $-196.4(\alpha)$, $-191.7(\gamma)$, and $-186.6(\epsilon)$ ²¹ are used and the entropy and heat capacity of γ - and ϵ -phases are assumed as the same with α -phase. Other values are taken from JANAF Thermochemical Table

and that of $\gamma\text{-Fe}_2\text{O}_3$ changes little with rise in reaction temperature. In the vapor phase oxidation of FeCl_2 in this temperature range, therefore, the nucleation of each phase, ϵ -, γ - and $\alpha\text{-Fe}_2\text{O}_3$, occurs independently, the transformation of ϵ - and $\gamma\text{-Fe}_2\text{O}_3$ into α -phase being considered to be small. At $1,000^\circ\text{C}$ where the yield of $\alpha\text{-Fe}_2\text{O}_3$ increases, there is a possibility of partial transformation of ϵ - or $\gamma\text{-Fe}_2\text{O}_3$ into α -phase.

On the oxygenolysis of FeCl_3 , the following results are obtained.

$[\text{FeCl}_3] = 2.0 \sim 2.3 \text{ vol}\%$, $[\text{O}_2] = 80 \text{ vol}\%$
 (balance; N_2).

Reaction temperature; 700°C 900°C

Intensity ratio 0.5 0.1

$(I_{(\alpha\text{-Fe}_2\text{O}_3, d=1.70)}/I_{(\gamma\text{-Fe}_2\text{O}_3, d=1.66)})$

The η -phase formed was completely transformed into $\alpha\text{-Fe}_2\text{O}_3$ by heating in air at 600°C for an hour. However, the yield of $\eta\text{-Fe}_2\text{O}_3$ at 900°C is greater than that at 700°C . In the oxy-

genolysis of FeCl_3 , accordingly, the nucleation of η - and $\alpha\text{-Fe}_2\text{O}_3$ also occurs independently.

The over-all reactions of FeCl_2 and FeCl_3 with oxygen are represented by eqs. (3) and (4), respectively.

It should be noted here that in the oxidation of FeCl_2 there may be formed a considerable amount of FeCl_3 by reaction between FeCl_2 and freed Cl_2 . The formation of FeCl_3 by eq. (5) is

favorable thermodynamically in the temperature range examined (Fig. 6). The oxidation of FeCl_2 should, therefore, be generally represented by

The ratio, $\text{Fe(II)}/\text{Fe(II)} + \text{Fe(III)}$, in diiron trioxide formed by arc discharge of iron electrodes is very small (0.57×10^{-3})²². The formation reaction is represented by

Of the formation reactions of Fe_2O_3 , eqs. (3) or (6) and (7) give metastable phases, ϵ - and $\gamma\text{-Fe}_2\text{O}_3$, and eq. (4) a metastable phase, $\eta\text{-Fe}_2\text{O}_3$. Eqs. (3) or (6) and (7) differ from eq. (4) in that the oxidation states of iron in the reactants are lower than those in the products. This suggests that the nucleation of ϵ - and $\gamma\text{-Fe}_2\text{O}_3$ is only possible when Fe(II) exists. The composition of ϵ - and $\gamma\text{-Fe}_2\text{O}_3$ clusters can be expressed by $\text{Fe(II)}_x\text{Fe(III)}_{2-x}\text{O}_3$. The structure of $\gamma\text{-Fe}_2\text{O}_3$ cluster may be similar to that of Fe_3O_4 . Although the nucleation of ϵ - and γ -phases requires the existence of Fe(II) , no tendency for yields of these two phases to increase as oxygen concentration decreases or FeCl_2 concentration increases was observed and the gas composition affects the yields of these metastable phases in a different way. In the oxidation of FeCl_2 , the yields of ϵ - and γ -phases change little or increase with oxygen concentration. Further, the yield of ϵ -phase is approximately constant and that of γ -phase decreases with FeCl_2 concentration. In the arc discharge method, ϵ - and α -phases increase and $\gamma\text{-Fe}_2\text{O}_3$ decreases as oxygen concentration increases²³.

The formation mechanism of Fe_2O_3 particles, then, needs further investigations.

The formation of ϵ - and γ - Fe_2O_3 in the oxidation of iron(II) chloride is observed only in the vapor phase reaction. When iron(II) chloride (mp. 677°C) was oxidized in the solid state (at 600°C) or in the liquid state (at 720°C) in O_2 of 1 atm for 5 min, the products were exclusively α - Fe_2O_3 . In the solid and liquid states, the cluster of ϵ - or γ - Fe_2O_3 , if produced, may state for a longer time at these high temperatures and be transformed into α - Fe_2O_3 structure. In the vapor phase oxidation, on the other hand, the clusters or particles produced leave the high temperature zone in a short time, resulting in the high yield of metastable phases.

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酸性水溶液中の鉄の腐食におよぼす交流の影響*

鳥 越 泰**

1 緒 言 (Introduction)

酸性もしくは中性水溶液中の鉄の腐食に関しては多くの研究によりその反応機構も明らかにされている反面、同環境下の交流腐食に関しては基礎的研究が少なく、その電気化学的挙動については解明されていない点が多い。中でも交流腐食の発生要因として重要な鉄の複合電極反応系に対する交流電流の作用については理論的^{1),2)}または実験的³⁾に追究されているが、現象が複雑であるためまだ体系的な考察は行なわれていない。

そこで本報では硫酸水溶液中の鉄の腐食が複合電極反応として進行する過程で、これに加わる微小交流電流が分極特性におよぼす影響を実験的に確かめ、合せて環境因子との関係について考察した。

2 実 験 (Experimental)

実験はおもに大気開放下の 0.1 M H_2SO_4 溶液 (液温

* 鉄の交流腐食に関する研究 (第1報) Studies on Alternating Current Corrosion of Iron (Part 1)

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Fig. 1 Experimental circuit

S_1 : DC Source, EC.: Electrolytic cell
 S_2 : AC Source, E_1 : Test electrode
 R_1, R_2, R_3 : Resistor, E_2 : Auxiliary electrode
 L : Choke coil, E_3 : Reference electrode
 C : Condenser, S.S.: Synchro-Scope
 A_1 : DC Milliammeter, P: Potentiometer
 A_2 : AC Microammeter

$20 \pm 0.2^\circ\text{C}$) 中の静止電極について行ない、また溶存酸素濃度の異なる各条件下で実験を補足した。おもな実験として交流成分を有する分極電流により鉄の分極特性を準定常法で求めた。その実験回路を Fig. 1 に示す。電源には直流電源と正弦波交流電源の並列回路を用いたが、