

# Analysis of Oxidation Behavior in Nanocrystal $\beta$ -FeSi<sub>2</sub>/Si Composites by Rutherford Backscattering Spectrometry and Computation of Diffusion Flux

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We have investigated oxidation behaviors of nanocrystal (NC)  $\beta$ -FeSi<sub>2</sub>/Si composites by Rutherford Backscattering Spectrometry (RBS) and computation of diffusion fluxes. The oxidation is controlled by diffusion of the O flux from the surface and the Si flux toward the Matano-Boltzmann (M-B) interface. The time dependence of the location of the M-B interface was determined. We proposed a model for oxidation of the composite that is different from oxidation of Si controlled by O diffusion through SiO<sub>2</sub> at the surface.

## 1. Introduction

Enhancement of photoluminescence from  $\beta$ -FeSi<sub>2</sub>/Si heterojunctions based on a confinement effect of electrons and holes in  $\beta$ -FeSi<sub>2</sub> nanocrystals of less than 10 nm in size have been reported [1]. Radiative recombination of electron-hole pairs excited is controlled by densities of electrons and holes in  $\beta$ -FeSi<sub>2</sub> potential wells with a band offset of the conduction band ( $\Delta E_c$ ) and that of the valence band ( $\Delta E_v$ ). From photocurrent measurements using the  $\beta$ -FeSi<sub>2</sub>/Si heterojunction, it was revealed that both band offsets were large enough to confine both electrons and holes in the  $\beta$ -FeSi<sub>2</sub> well, however, the  $\Delta E_v$  became too small to confine the holes [2]. This knowledge teaches that almost the holes may be thermally activated and they escaped to outside of the well, when the temperature increased. The  $\Delta E_v$  for holes becomes near zero at room temperature. This situation supports the fact that room temperature light emission is very small or limited. From above consideration, we have looked for an appropriate heterostructure with large band offsets for both bands in which the electrons and holes can be effectively confined. One of candidates is a  $\beta$ -FeSi<sub>2</sub>/SiO<sub>2</sub> heterojunction, which may be easy to synthesize from  $\beta$ -FeSi<sub>2</sub>/Si heterojunctions by sample oxidation. Nakamura et al. have reported synthesis of nanocrystal  $\beta$ -FeSi<sub>2</sub> (NC- $\beta$ ) embedded in SiO<sub>2</sub> by using oxidation of samples in air, and they succeeded in observation of evident photoluminescence at 250 K [3]. Moreover, Morita et al. [4] have reported time dependent growth of SiO<sub>2</sub> in oxidation of  $\beta$ -FeSi<sub>2</sub>/Si, and they found no structural and quantitative changes of NC- $\beta$  by using infrared absorption (IRA) measurements, and pointed that selective oxidation took place in the sample. These reports indicate that the oxidation process is effective to synthesize  $\beta$ -FeSi<sub>2</sub>/SiO<sub>2</sub> heterojunction with enough large band offsets for electrons and holes even above room temperature from the  $\beta$ -FeSi<sub>2</sub>/Si heterojunction.

In this study, toward development of higher control of sample oxidation, oxidation behavior in Si layers composited with NC- $\beta$ -FeSi<sub>2</sub> was investigated by Rutherford backscattering spectrometry (RBS) and computation of diffusion flux using elements depth profiles that was deduced from RBS.

## 2. Experiments

Precursor samples including NC- $\beta$  (the average size less than 10nm) embedded in Si were synthesized by an ion beam synthesis (IBS) process. Oxidation of the sample was carried out at 900 °C in an electrical furnace



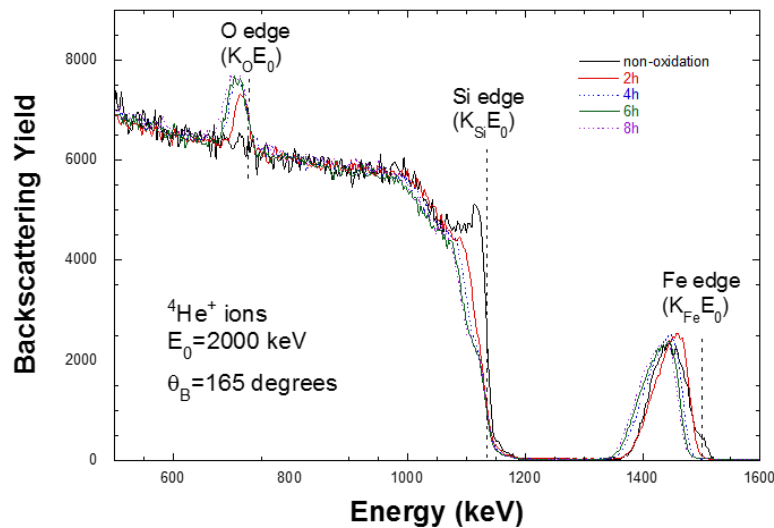
in circulating dry air. Formation of NC- $\beta$  was confirmed by far-IRA measurements. 2.0 MeV- $^4\text{He}^+$  Rutherford Backscattering Spectrometry (RBS) were measured at the backscattering angle of  $165^\circ$ . For the energy calibration of each channel, high purity Fe plates, Si wafers, Al foils, Au films were employed. Depth profiles of elements compositions were deduced from random RBS spectra by SIMNRA<sup>®</sup> [5]. A diffusion fluxes  $J_i$  of element  $i$  in depth after oxidation duration  $t$  were computed by the following equation composited in *MultiDiFlux* distributed by Dayananda of Purdue University [6].

$$J_i = \frac{1}{2t} \int_{c_i}^{c(x)} (x - x_0) dc_i$$

where  $x_0$  is the location of the Matano-Boltzmann plane and  $c(x)$  is a concentration of each element at depth  $x$ .

### 3. Results and Discussions

Figure 1 shows random RBS spectra of the samples oxidized for each times. It was observed that Fe spectrum near the Fe edge at  $K_{\text{Fe}}E_0$  shifted to the lower energy, however, the width of spectrum indicated small change. Growth of silicon oxide near the sample surface was confirmed from increase of both the yield and the width of oxygen spectrum near  $K_{\text{O}}E_0$ .

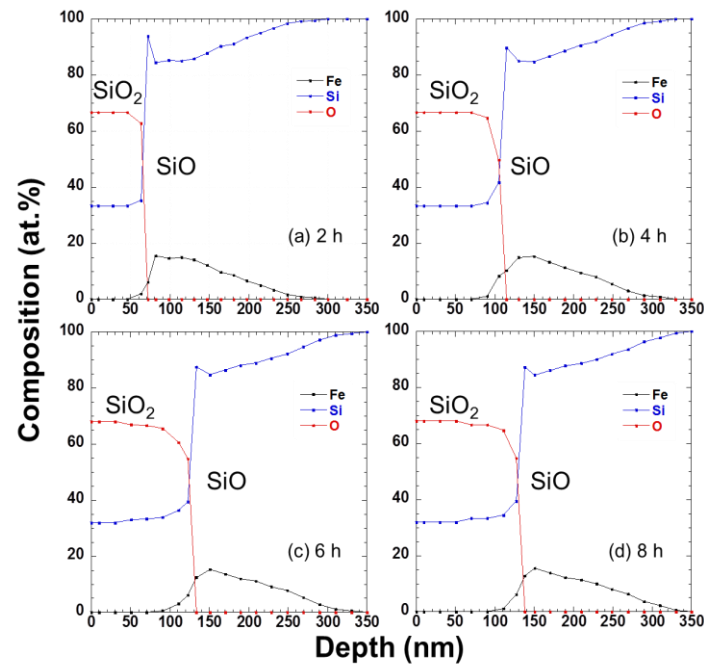


**Fig. 1.** Random RBS spectra of the NC- $\beta$ /Si composite oxidized for each times. After the oxidation, the oxygen (O) spectrum at the O-edge  $K_{\text{O}}E_0$  appeared on the base of Si spectrum.

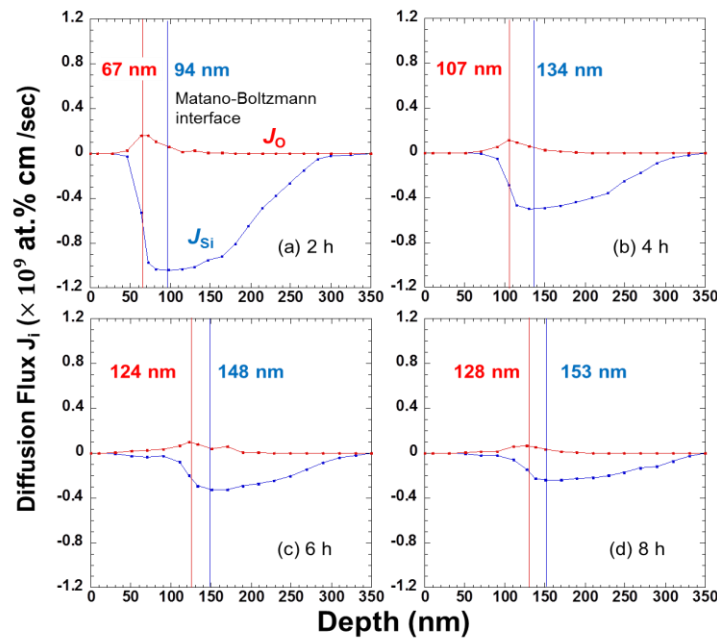
Using SIMNRA analysis of these random RBS spectra, we obtained details of depth profiles of Fe, Si and O for each samples oxidized for 2-8 h as shown in Figs.2 (a)-(d). Growth of  $\text{SiO}_2$  near the surface was observed with increasing the oxidation time. Such an apparent shift of Fe distribution toward the deeper location was caused by growth of  $\text{SiO}_2$  with 2.6 times of volume expansion at the sample surface.

As an interesting fact, it was found that the composition at the interface between Si and O atoms was fixed at the composition ratio of Si/O=1 during the oxidation. This fact may be a new finding for a conventional oxidation process of Si. The reason has not been solved, however, presence of Fe implants may affect the oxidation process of Si. Quantitative discussion requires details of element diffusion behaviors. The diffusion fluxes of Si and O and their time dependence were computed.

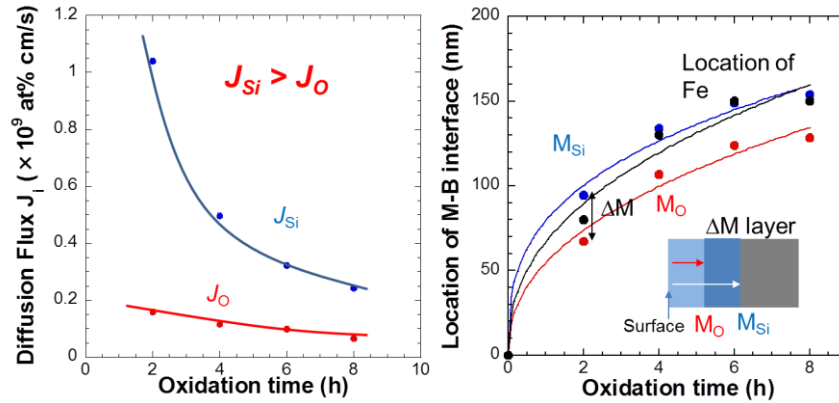
Figures 3 (a)-(d) show diffusion fluxes computed from each depth profiles. These results indicated that the oxidation process in this composite was controlled not only by diffusion of oxygen from the surface but also by diffusion of Si atoms from the composite. The Matano-Boltzmann (M-B) interface for interdiffusion of Si and O atoms shifted systematically toward deep portion with increasing the oxidation time. This M-B interface zone between red and blue lines in Fig. 3 can be understood as the meeting place for Si and O atoms diffused from each sides.



**Fig. 2** Depth profiles of Fe, Si and O atoms deduced from their random RBS spectra by using the SIMNRA code [5]. The times for sample oxidation in dry air at 900°C were 2-8 hours. The Fe depth profile indicated small change with increasing the oxidation time. This fact suggests that Fe atoms in the iron silicide does not contribute to the oxidation process. At the interface between the oxide and the silicide at the front edge of Fe profile, the oxide layer with oxygen deficiency such as  $\text{SiO}_{2-x}$  was formed. This behavior will be discussed later by using results of Figs. 4 and 5.



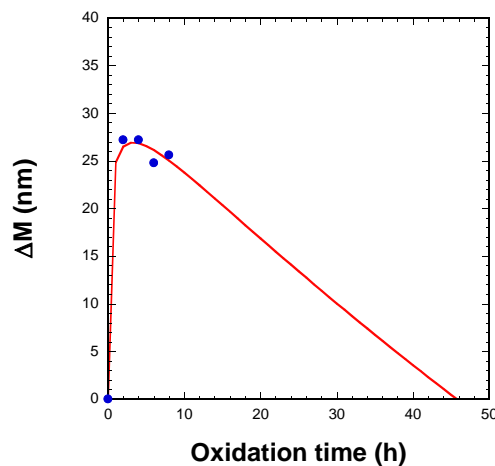
**Fig. 3** Changes of diffusion fluxes of Si and O atoms when the oxidation time increased. The plus sign means diffusion direction from the surface to the deep portion, and the minus sign means a contrary diffusion direction. The Matano-Boltzmann interfaces indicated by red and blue lines are indicated for Si and O fluxes, respectively.



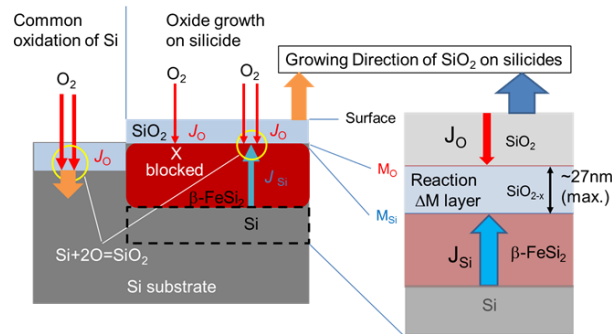
**Fig. 4** (left) Matano-Boltzmann (M-B) interfaces for Si and O atomic fluxes computed from diffusion fluxes shown in Figs.3 (a)-(d). In the right figure, the difference in location between their M-B interfaces ( $\Delta M$ ) is  $\sim 27$  nm which is associated with difference in their diffusion fluxes.

In comparison with oxidation of Si which is limited by diffusion of O atom in  $\text{SiO}_2$ , this oxidation behavior obtained from this analysis may be quite unique.

Figure 4 (left) shows changes of the diffusion flux as a function of the oxidation time. It was found that the Si flux  $J_{\text{Si}}$  decreased rapidly after oxidation for 2 h, then approached the oxygen flux  $J_{\text{O}}$ . Figure 4 (right) shows the location (or depth) of the Matano-Boltzmann interfaces from the surface of growing oxide. The Si interface was deeper than the oxygen interface, and their locations did not become same when the oxidation time increased. The location of the M-B interface  $d_{\text{M-B}}$  (nm) for each fluxes was fitted as a function of the oxidation time. We obtained  $d_{\text{M-B}}(\text{Si}) = 79.61t^{0.33}$  and  $d_{\text{M-B}}(\text{O}) = 54.75t^{0.43}$  ( $t$  is the oxidation time in hour) for Si and O fluxes, respectively. The exponent of O diffusion flux has larger than that of the Si diffusion flux, and the preexponential factor of O diffusion flux has smaller than that of the Si diffusion flux. This time dependence is close to that observed by IRA [3]. This result can be understood from a big difference in amount of diffusion fluxes between Si and O atoms as shown in Figs.3 (a)-(d). As shown in Fig.4 (right), the difference in their location between each interfaces is defined as  $\Delta M$ . The  $\Delta M$  for 2 h oxidation was about 30 nm in thickness. The  $\Delta M$  layer with  $\Delta M$  in thickness can be considered to be the portion in which Si and oxygen fluxes meet together. Si atoms are supplied into this  $\Delta M$  layer more than oxygen atoms, therefore, this layer becomes an oxygen deficient oxide such as  $\text{SiO}_{2-x}$ . The time dependence of  $\Delta M$  is given by  $\Delta M = d_{\text{M-B}}(\text{Si}) - d_{\text{M-B}}(\text{O}) = 79.61t^{0.33} - 54.75t^{0.43}$ . Figure 5 shows the observed (blue dots) and estimated (red curve)  $\Delta M$  values as a function of the oxidation time. The  $\Delta M$  value becomes the maximum at 2-3 h for oxidation, then decreases. After oxidation for 45-46 h, at least the  $\Delta M$  is estimated to be zero in thickness.



**Fig. 5** Thickness of the  $\Delta M$  layer as a function of the oxidation time. The blue dots are observed and the red curve is calculated from the equation  $\Delta M \text{ (nm)} = 79.61t^{0.33} - 54.75t^{0.43}$ , where  $t$  is the oxidation time in hour.



**Fig. 6** Schematics of difference in oxidation behaviors on Si substrates and on silicides. The two yellow circles indicate points where the reaction  $\text{Si} + 2\text{O} = \text{SiO}_2$  proceeds. The right figure shows a detail structure around the silicide and the oxide layers, and Si and oxygen fluxes that made the  $\Delta M$  layer (the maximum thickness  $\sim 27$  nm) with oxygen deficiency as indicated in Fig. 5.

This behavior obtained in Fig. 5 may be attributed to pronounced decrease in the Si flux  $J_{\text{Si}}$ , when growth of oxide from the sample surface proceeds.

Figure 6 shows schematics of difference in oxidation behaviors on Si substrates and on the silicide obtained in this study. In the left figure, you can see the Si flux from the Si substrate and goes through the silicide and onto the silicide surface, also the oxygen flux comes from air into the surface oxide. Oxidation of Si is dominated by the oxygen diffusion in the oxide and reaction rate. In contrast, in silicide/Si composites the Si flux coming through the silicide layer and onto the surface dominates the growth of Si oxide layer on the silicide, because the oxygen flux is blocked by the silicide layer and cannot go through the silicide. Figure 6 (right) shows a detail of layer structures deduced from the M–B interfaces and diffusion fluxes. There is a difference in the M–B interface of Si and oxygen fluxes. The Si atoms are supplied into this intermediate layer denoted by the  $\Delta M$  more than the oxygen atoms, so that the  $\Delta M$  layer becomes an oxide layer with oxygen deficiency. However, from analysis in Fig. 5, we estimate to synthesize non oxygen deficient oxide after sample oxidation for 45–46 h.

#### 4. Conclusion

We have investigated oxidation behaviors of NC- $\beta$ /Si composites by RBS and computation of diffusion flux. The oxidation is controlled by diffusion of O atoms from the surface and that of Si atoms toward the Matano-Boltzmann (M–B) interface. The time dependence of location of the M–B interface was determined. This oxidation situation is far from oxidation of Si controlled by O diffusion through  $\text{SiO}_2$  at the surface. We have proposed the oxidation model for the composite and known that the composite cannot be fully oxidized even after oxidation for 8 h. Further long time oxidation reaching 45–46 h may be required to obtain fully oxidized composites.

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