Application of x-ray reflectivity measurement to monitoring of chemical reactions at 'buried' interface

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Abstract. A metal/yttria interface reaction by low temperature treatment at 100 °C was chased by X-ray reflectivity measurement (XRR). Since the soft reaction did not affect surface morphology, it was not detectable by atomic force microscopy. The XRR results indicated that the structural change at Au/Y2O3 interface was more significant than Pr/Y2O3. This difference can be explained by non-oxidization property of Au; the Au/Y2O3 interface easily releases O atom, resulting in instability at the interface. The soft reaction of metal/Y2O3 would be applicable to post-formation of nano-interface structures. For electronic device applications, since monitoring of microscopic reaction is mandatory, μ-XRR should be developed.

1. Introduction
In recent years, interface chemical reactions are considered to be applicable for data storage [1]. Since quasi-stable chemical states correspond with the on/off states in memory devices, quick alternation of the chemical states should be compatible with high frequency switching (Fig. 1(a)). As another advanced example, a selective reaction at buried interface can be used for durable data printing in media, post-formation of nano-structures in layer structures, holographic memory etc (Fig. 1(b)). For these attractive applications, we are focusing on oxidization-reduction at metal/oxide interfaces. In fact, the interface reaction related with oxygen bustling yields memory effect, and it has already been applied to non-volatile memory devices [2]. Moreover, controllability and stability of oxides are suitable for the post-formation of microstructures at buried interface.

X-ray reflectivity (XRR) measurements can non-destructively provide structural information of multilayer with high depth resolution < ~nm [3]. This potential ability suggests the applicability of XRR to evaluation of interface...
reactions. Now, what we want to know is the sensitivity of the XRR measurements to the interface reactions. In this study, we evaluated soft reactions at metal/yttria (Y$_2$O$_3$) interface by XRR.

2. Experiments

The interface structure was fabricated by following procedure. Y$_2$O$_3$ was formed on Si (100) wafer with a metalorganic decomposition method (MOD coat, Kojundo Chemical Laboratory Co., LTD.). On the Y$_2$O$_3$ thin layer, Pt or Au as the metal was deposited by a sputtering. The thicknesses of Y$_2$O$_3$ and metal were ~50 and ~30 nm, respectively. The Pt/Y$_2$O$_3$ and Au/Y$_2$O$_3$ interface reactions were thermally induced in a furnace, and were evaluated by XRR. We also carried out in-plane x-ray diffraction (XRD) and atomic force microscopy (AFM) for thin film evaluation. For the XRR and XRD measurements, we used RINT-ATX (Rigaku Corporation, UltraX18 and in-plane goniometer). AFM for evaluation of surface morphology was performed with SPM9500-J3 (Shimadzu Corporation).

3. Results and discussions

3.1. High temperature reaction process of Y$_2$O$_3$/Si

Prior to observation of the reaction at the metal/Y$_2$O$_3$ interface, we point out that crystallization process of the Y$_2$O$_3$ thin film on Si wafer is a good touchstone of the ability involved in XRR.

As mentioned above, we used the MOD coat to make the Y$_2$O$_3$ thin film on Si wafer. In the MOD process, a metalorganic solution including Y and O dropped on the Si wafer, and the droplet was spread over by a spin coater. After 2 min drying at 120 °C, the coated network of Y and O was crystallized to Y$_2$O$_3$ film by annealing at 550 °C in a furnace. Here, we chase the crystallization process at high temperature by XRR. Figure 2(a) indicates XRR of Y$_2$O$_3$/Si dependent on the annealing time. The data is displaced vertically with increasing annealing time. As shown in this figure, XRR was continuously changed with respect to the annealing time; the oscillation is abruptly amplified at 30min and after that it is gradually lessened. Finally, it is completely disappeared after annealing for 90 min.

Corresponding in-plane XRD data set is shown in Fig. 2(b). In these measurements, x-ray incidence angle $\theta$ was fixed at 0.35° and 2$\theta$ scanning was performed for probing diffracted x-rays from the surface layer. From this surface sensitive XRD, we can understand the actual crystallization process of Y$_2$O$_3$ thin layer on the Si wafer. The diffraction peaks from Y$_2$O$_3$ crystal are gradually strengthened and are not built up after 30 min any more; the crystallization was completed at 30min.
Note that XRR in Fig. 2(a) provides surface dynamics different from XRD in Fig. 2(b). Interestingly, the combination analysis of macroscopic measurements XRR and XRD provides a microscopic model on the sample surface. Now, we propose a two-step surface process during the high temperature annealing as follows.

First, although XRD showed that Y$_2$O$_3$ began to crystallize right after the temperature rising (Fig. 2(b)), XRR indicated that the Y$_2$O$_3$/Si interface abruptness was established just on 30min (Fig. 2(a)). This finding reveals that the crystallization is started in places; in the early stage of the annealing, micro-crystals are scatteringly formed, so that they cannot make uniform and abrupt interface. As the annealing progresses, the growing micro-crystals meet up, resulting in the abrupt Y$_2$O$_3$/Si interface. This model indicates that the Y-O network before the Y$_2$O$_3$ crystallization is not appropriate for the abrupt interface.

Second, although XRD profile was not changed by the annealing longer than 30 min (Fig. 2(b)), XRR indicated that the layered structure continuously degenerated by the long annealing (Fig. 2(a)). This result suggests the growing micro-crystals do not make a single domain by bunching, yielding large stress at the domain boundary. The large stress forces up the domains, resulting in rough interface and/or surface of Y$_2$O$_3$.

Actually, surface analysis by AFM traces the annealing model. Figure 3 shows surface roughness in rms. (root mean square) during the annealing. The shorter annealing flattens the Y$_2$O$_3$ surface as denoted by region I. It corresponds to meeting up process of the grain (The first step). On the other hand, the longer annealing indicated by region II roughen the Y$_2$O$_3$ surface. It corresponds to the force up process of the rushing domains (The second step).

In this high temperature annealing process, the combination analyses of XRR, XRD, and AFM successfully provided the crystallization model. However, it is not indicates any advantages of XRR compared with XRD and AFM. From various researches, it is no wonder that XRR can see the hard reaction process. In order to indicate worth of XRR, we observed a soft reaction process of metal deposited systems, Pt/Y$_2$O$_3$ and Au/Y$_2$O$_3$.

3.2 Low temperature reaction process of Metal/Y$_2$O$_3$ interface

For fabrication of the metal/Y$_2$O$_3$ interface, the metal, Pt or Au, was deposited by an RF sputtering on Y$_2$O$_3$ prepared by the process described in 3.1. The annealing time for the Y$_2$O$_3$ crystallization was fixed at 30min. After the metal deposition on Y$_2$O$_3$, we performed low temperature treatment at 100°C in N$_2$ ambience, and observed the metal/ Y$_2$O$_3$ interface reaction by XRR.

Figure 4(a) indicates XRR of Pt/Y$_2$O$_3$ with respect to the thermal treatment time. For clarity, the data are shifted up by 10$^2$ vertically with increasing treatment time. From careful observation, it can be seen that the treatment shorter than 90 min amplifies the XRR oscillation. On the other hand, the treatment longer than 90 min lessens the oscillation. This tendency can be confirmed with Fourier transform (FT) of the XRR oscillation more clearly. The peak amplitude of FT versus the thermal treatment time is illustrated in the inset of the Fig. 4(a). This peak amplitude has the maximum at 90 min which corresponds to the turning point of XRR oscillation described above.

Similar experiment was performed for the Au/Y$_2$O$_3$ system. Figure 4(b) summarizes the XRR oscillation of Au/Y$_2$O$_3$ dependent on the treatment time as well as Fig. 4(a). From the inset of Fig. 4(b) illustrating the peak amplitude of FT of XRR, it is understood that the largest XRR amplitude is obtained at the treatment for 60 min shorter than the Pt/Y$_2$O$_3$ case (90min) described in Fig. 4(a).
Another difference between Pt/Y₂O₃ and Au/Y₂O₃ can be seen in the XRR oscillation profile such as period. As shown in Fig. 4(a), during the treatment of Pt/Y₂O₃ system, the XRR oscillation profile was unchanged. On the other hand, the XRR profile of Au/Y₂O₃ is continuously changed with increasing treatment time as shown in Fig. 4(b). We have never identified the interface structure reproducible the XRR profile. However, the difference of these systems would be caused by different reactivity of Pt and Au with O. Pt can react with O, resulting in Pt oxides such as Pt(OH)₂, PtO₂, and YOOH. In spite of another possibility of metal-alloy formation at the Pt/Y₂O₃ interface, x-ray photoemission spectroscopy indicated that these Pt oxides can be produced easily at the interface. On the other hand, since Au does not make oxides, O would be released from the interface. The O release results in unstable interface, i.e., more significant change by the thermal treatment.

Interestingly, the low temperature reaction process observable by XRR cannot be sought out by in-plane XRD and AFM. Figure 5 shows surface roughness in rms. during the thermal treatment evaluated from AFM images. The typical AFM images of Pt/Y₂O₃ and Au/Y₂O₃ surfaces (scanning area: 2µm × 2µm, full scale in height: 7 nm) are shown in the insets of this figure. From this figure, it was found that both of the systems Pt/Y₂O₃ and Au/Y₂O₃ kept atomically flatness, ~0.82 nm for Pt (open circles) and ~0.65 nm for Au (closed circles). We also comment that the interface reaction was undetectable by in-plane XRD; the reaction layer is considered to be sufficiently thin.

The surface images obtained by AFM provide microscopic roughness in ~μm² area, so that it is not always equal to the macroscopic roughness in ~mm² area evaluated by XRR. However, these results indicate superiority of XRR to AFM and XRD for
the monitoring of soft reactions at interfaces.

These results infer that the low-temperature thermal treatment of the metal/Y₂O₃ systems is applicable to the post-formation process as described in Fig. 1(b). In this artificial process, a selective interface reaction without surface modification is required. Figure 5 indicates no surface modification within the detection limit of AFM. The post-formation at buried interface can be realized by the low temperature treatment of metal/Y₂O₃. The thermal process using a scanning thermal spot such as a laser beam would form micro decorations at the interface.

4. Summary
For high density data storage, nm-scale structures built in layered structures are promising. Selective interface reaction due to external perturbations can make the built-in structures without complicated processes. Moreover, some atomic-scale interface reaction can provide quasi-stable states corresponding with on/off states and it must be used for a non-volatile memory. The interface reactions should be a soft process keeping surface flatness. We observed the soft interface reaction in metal/Yttria systems by x-ray reflectivity (XRR) measurement, and differentiated the reactivity of Au and that of Pt.

In the actual application to electronic devices, the soft interface reaction should be induced within nn area. This trend strongly demands development of μ-XRR with high lateral resolution.

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