Epitaxially Grown Microcrystals in Thermally Oxidized Amorphous SiO₂ Film on Si(001) Wafers

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Epitaxially grown microcrystals in amorphous SiO_2 thin-film on Si(001) substrate was investigated by using X-ray crystal truncation rod(CTR) scattering. It was found that microcrystals exist in amorphous layers of all the samples investigated, which include both samples oxidized at low and high temperature. The distribution function of the crystallites and its crystal structure suggest that such a crystalline phase is a result of an intrinsic strain at the interface, caused by the large volume expansion followed by the oxidation of the Si(001) surface. The relationship between the crystallization and interface morphology was discussed.

Structure of amorphous SiO_2 thin-film grown on a Si wafer has been attracted much attention because of its many interesting electrical and mechanical properties. In order to clarify the interface morphology and the structure of the amorphous SiO_2 layer grown on Si(001) wafers, measurements of X-ray crystal truncation rod(CTR) scattering were performed by the present authors and others^{1,2}. The experimental results so far obtained can be summarized as follows².

1) Extra peaks consisting of a main and several sub peaks are observed on the low angle side of the 111 CTR scattering from the Si(001) substrate of which surface was thermally oxidized at 960– $1000^{\circ}C$ (Figure 1, 2). The same kind of peaks are also found by so-called Wet-O₂ samples, as well as p-type silicon and n-type silicon.

2) The main peak is located on the (1,1,q) (q is about 0.46), and on the other equivalent points such as the (-1,1,q) point in reciprocal space. We call the main peak the 11q reflection hereafter.

3) The width of the 11q reflection in the direction normal to the [001] is as small as that of the 111 Bragg reflection from the Si substrate.

4) Integrated intensity of the 11q reflection is almost proportional to the thickness of the amorphous SiO₂ layer and the reflection is not detected in the sample of which surface was etched by HF solution.

5) The period of the interference fringes in the direction perpendicular to the crystal surface corresponds to the inverse of the thickness of the amorphous SiO_2 layer.



Figure 1 Bragg points of Si, CTR scattering and 11q reflection in reciprocal space.



Figure 2 111 CTR scattering of Si(001) plane oxidized at 960 $^{\circ}$ C. The nominal thickness of the oxidized film is about 250 Angstrom. The line is a guide for eyes.

2) and 3) indicate that the scatterer is not an amorphous-state but a single crystalline phase. On the other hand 4) and 5) manifest the scatterer exists in the amorphous layer. In order to explain all the above results consistently, a model of the amorphous structure was proposed: many microcrystals are distributed in the amorphous layer by keeping an epitaxial relation with the Si(001) substrate. The least squares analysis was successfully performed based on this model²). This must be the first evidence on naturally-grown epitaxial crystallites in amorphous SiO₂ layers, although there have been several reports on the crystalline state which exists on the interface between the Si substrate and the amorphous layer^{3,4,5)}. Our understanding on the growth mechanism of the peculiar amorphous structure is far from sufficient: how do the crystallites grow?; why is such a weird crystal structure stable?; are there any special condition in forming the epitaxial relationship? etc..

In order to try to answer above questions and to have better understanding of the growth mechanism of the amorphous SiO₂ layer, we studied several samples prepared under various conditions. The samples were as follows: oxidized at 650° C in O₃ atmosphere, thickness of the amorphous layer=125 Angstrom(O_3 oxidation); oxidized at 650° in the atmosphere of afterglow of microwave plasma of oxygen molecule(abbreviated as AGMP oxidation), thickness=70 Angstrom; oxidized at 900℃ in dry flow, thickness=112 Angstrom($Dry-O_2$) O_{2} oxidation). A rotating anode X-ray generator and synchrotron radiation source(BL-4C, BL-6A2, Photon Factory, KEK, Japan) were used for preliminary study and the study with high resolution, respectively. The details in the CTR scattering measurement were described in the previous study²⁾.



Figure 3 Low angle side of CTR scattering near the 111 Bragg point in 00l direction. The symbols are shown in the text.

The 11q reflection was detected by all the samples (Figure 3). However as shown in the figure, the profile and intensity of the 11q reflection strongly depend on the oxidation condition of the substrate. Therefore a quantitative analysis of the present data would bring us a deeper understanding of the oxidation of the Si(001) surface.

In order to proceed to further analysis, crystal structure and the distribution function of the crystallites should be elaborated. We adopted the pseudo-cristobalite structure, which was the same as that used in the previous study^{1,2,5)}. As for the distribution function of the crystallites in the amorphous layer, so-called modified exponential decay model(MoEXP Model) was also adopted which was found to be appropriate for the high temperature oxidation sample in the previous study²⁾,

 $\begin{array}{ll} \rho(z) = \rho_1 + \rho_0 & (z=1) \\ \rho(z) = \rho_1 exp(-zc/\xi) & (z=2,3,..P_{\max}), \end{array}$

where $\rho(z)$ represents the probability of finding the crystallites at height z, which is the distance from the interface in the unit of the lattice parameter $c(=a_{si}/q)$ of the pseudo-cristobalite crystal. In addition to the above parameters and the structural parameters like temperature factors, parameters describing the interface morphology would be considered. As for the parameter of this kind, we only treated an interface roughness parameter of a Gussian-type for simplicity⁶). All the solid curves in Figure 3 show the calculated values obtained by least squares calculations based on the present model. The agreement between the observations and the calculations seems to be quite satisfactory. The refined parameters and R-factors are listed in Table 1.

Table 1 R-factors and refined parameters. Lattice parameter of the pseudo-cristobalite crystal c, ξ and the roughness parameter $\langle P^2 \rangle$ are shown in Angstrom unit. Since the $P_{\rm max}$ of AGMP is 2, only ρ_0 and ρ_1 were refined, namely it is equivalent that ξ was put to be infinity. The E.S.D. of the refined parameter is written in the parentheses.

The success of the present MoEXP Model seems to suggest us a plausible mechanism of the formation of amorphous SiO_2 layer in which the pseudo-cristobalite crystallites are embedded. The oxidation occurs at the interface; oxygen is constantly supplied throughout the diffusion into the amorphous SiO_2 layer. Thus it would be reasonable for us to suppose that the crystallites are mainly formed at the interface. Certain area of the Si(001) surface is covered with the crystallites; according to the refined parameters, the coverage is less than $10\%(=100\times(\rho_0+\rho_1))$). By further oxidation, the interface itself proceeds to interior of the substrate; some of the crystallites still remain at the positions where they were synthesized, the others may decay and transform to the amorphous state. That would be the reason that the distribution at the interface(z=1) is almost twice as large as that at z=2, and it decreases with increasing the distance from the interface. Origin of the instability of the crystallites is not clear, but we may be allowed to consider that the crystallites of such an unusual structure is a result of a severe strain at the highly mismatched interface, produced by the large volume expansion followed by the oxidation. Therefore the crystallites may become unstable at a large z.



Figure 4 Schematic illustration of the amorphous layer. $a-SiO_2$ and $c-SiO_2$ represent the amorphous SiO_2 phase and the cryatal SiO_2 phase(microcrystals), respectively.

It is noticeable that the probability of the low temperature oxidation samples is less than that of the $Dry-O_2$ oxidation sample. In the case of the AGMP sample, the crystallites are few and appear to localize at the interface. Thus the atmosphere for the oxidation is quite important. The roughness parameter shows an interesting feature. The interface of the $Dry-O_2$ oxidation is smoother than the case of the two kind of low temperature oxidation samples investigated here. Therefore we may deduce that the interface roughness has an inclination toward the amorphous state. Other refined parameters also would help us to understand the nature of the crystallization and the oxidation process, and the details will be published in near future.

Dependence of the crystallization on the interface strain would be an interesting problem which should be studied by a further experiment with mechanically-stressed or annealed samples and samples oxidized at different temperatures in the same atmosphere. Relationship between the crystallites and the mechanism of electrical breakdown of the amorphous SiO_2 film is also very important.

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