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<td>Horita, Susumu; Akahori, Tetsuya</td>
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Description
Effect of the Crystallization-Induction Layer of Yttria-Stabilized Zirconia on the Solid State Crystallization of an Amorphous Si Film

Susumu Horita* and Tetsuya Akahori
School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Ishikawa 923 – 1292, Japan
E-mail: horita@jaist.ac.jp

Abstract

We investigated the crystallization-induction (CI) effect of yttria-stabilized zirconia (YSZ) on the solid phase crystallization of amorphous Si (a-Si) films. The incubation time $\tau_i$ for crystallization on a polycrystalline YSZ layer was shorter than that on a glass substrate. From the result of Arrhenius plots of $1/\tau_i$, it is suggested that the CI effect is not due to the difference in the activation energy $E_i$ but to a higher nucleation site area density on the YSZ layer. Also, preheating the YSZ layer prior to a-Si film deposition was effective to shorten the incubation time $\tau_i$ because $E_i$ was reduced.
Polycrystalline silicon (poly-Si) TFTs have great advantages of higher stability or reliability and higher mobility. Since the demands for applications of poly-Si TFTs are low-temperature fabrication, low cost, and high performance, several methods to fabricate poly-Si films have been proposed, such as solid phase crystallization (SPC),1,2) metal-induced crystallization (MIC),3,4) metal-induced lateral crystallization (MILC),5,6) pulse laser annealing (PLA)7-9), etc.10,11) However, each individual method has some drawbacks such as a high process temperature, a long annealing time, remnant metal as a leakage current source, non-uniform device performance, and so on.

So far, in order to obtain a poly-Si film with a uniform electrical property in fabrication conditions of both a short time and low temperature, we have proposed a crystallization-induction (CI) layer method using yttria-stabilized zirconia [(ZrO$_2$)$_{1-x}$(Y$_2$O$_3$)$_x$ : YSZ] as a CI material.12,13) In this method, an amorphous Si (a-Si) film is deposited on a YSZ layer that covers the surface of a substrate. Since YSZ has a small lattice mismatch of ~ 5% and the same cubic crystal structure as Si, it can be expected that a poly-Si film thus obtained has a uniform grain size and crystallographic orientation, owing to crystallographic information of the YSZ layer. Actually, we produced a crystallized Si film by directly depositing on a polycrystalline YSZ (poly-YSZ) layer at the substrate temperature of 320 °C, which was ~ 100 °C lower than that on the glass substrate without the YSZ layer.13) However, the surface of directly deposited poly-Si films is generally much rough, compared with SPC poly-Si films.1) So, for a reduction of the surface roughness of crystallized Si films, we tried to crystallize an a-Si film in the solid phase on a poly-YSZ layer by furnace annealing.

In this study, we focus on the CI effect of the poly-YSZ layer on the SPC of a-Si film and investigate it, and the results are compared to those obtained with a glass substrate.
without the YSZ layer and a single crystal (111)-oriented YSZ substrate as an underlying substance. Since the cleanness of a deposition surface is important for Si film growth on it, we also tried to heat a poly-YSZ layer in a deposition vacuum chamber just before Si film deposition, in order to remove out contaminants absorbed on the sample during loading. Hereafter, this heating process is called preheating. In the paper, we present the investigation results and discuss them, in particular, from the viewpoints of thermodynamic activation energy and nucleation density of the CI layer of the YSZ.

Figure 1 shows the schematic diagrams of the three kinds of sample structures, (a) a-Si film deposited on a poly-YSZ film which covers the surface of a fused quartz substrate (Si/poly-YSZ/glass), (b) a-Si film deposited on a single crystal (111)-oriented YSZ substrate (Si/(111)-YSZ), and (c) a-Si film deposited on a fused quartz substrate (Si/glass). A fused quartz glass substrate (10 × 20 mm²) is chemically cleaned before deposition of a poly-YSZ layer at a substrate temperature of 50 °C by reactive magnetron sputtering. Ar and O₂ are used as sputtering and reactive gases, respectively, with a sputtering pressure of ~ 6.5 mTorr.¹⁴) By X-ray diffraction measurement, it is found that the YSZ layer is preferentially (111)-oriented. This is a main reason why the orientation of the single YSZ substrate is (111). The chemical composition of Y/(Zr+Y), \( R_Y \), in the deposited YSZ layer is estimated to be about 19% by X-ray photoelectron spectroscopy measurement. Before deposition of an Si film, the YSZ layer is chemically cleaned, using a procedure described in the previous report.¹³) Then, a 60-nm-thick a-Si film is deposited on a YSZ/glass substrate with an e-beam evaporation method at 300 °C at a pressure less than \( 2 \times 10^{-8} \) Torr. For comparison, a-Si films are deposited directly on a single (111)-oriented YSZ substrate with an \( R_Y \) of 23 % and a glass substrate without
YSZ layer, individually. Also, just prior to Si film deposition, some of the poly-YSZ/glass samples are heated at 500 °C for 10 or 60 min in the Si deposition chamber at around the deposition pressure. Subsequently, crystallization of a-Si film is performed by annealing in an electric furnace at a temperature $T_A$ of 560, 570, or 580 °C in a N$_2$ atmosphere. The crystallization degree of Si films is estimated by Raman spectroscopy using a He-Ne laser beam (632.8 nm). The crystalline fraction, $X_c$, is determined by the empirical expression $X_c = (I_c + I_m)/(I_c + I_m + \sigma I_a)$, where $I_c$, $I_m$, and $I_a$ are the integrated intensities corresponding to crystalline, intermediate, and amorphous component peaks, respectively, and $\sigma$ is the ratio of the integrated Raman cross section for the amorphous phase to that for crystalline phase. In this study, $\sigma$ is chosen to be 1 for simplicity.\textsuperscript{15,16} Depth profiles of Zr and Y in a crystallized Si film are measured by secondary ion mass spectrometry (SIMS).

Figures 2 (a), (b), and (c) show the Raman spectra for the three kinds of samples, where the annealing time is a parameter. In Fig. 2(b), a broad and large peak around 600 cm$^{-1}$ is due to the single crystalline substrate of (111)-YSZ. As can be seen from Figs. 2 (a) and (b), small Si peaks appear at $\approx$520 cm$^{-1}$ due to crystalline Si (c-Si) at the annealing time $t_a$ of 775 min. However, in Fig. 2 (c), without the YSZ layer, there is no c-Si peak at the same $t_a$ but, after $t_a = 1000$ min, a small peak of c-Si is observed. This indicates that a-Si films on YSZ crystallize more quickly than without YSZ, probably because of the CI effect of YSZ. After an annealing of about 1000 min, the crystallization shows a saturation tendency, except for (c) without YSZ.

Figure 3 shows the annealing time dependences of crystalline fractions $X_c$ of the Si films deposited on a poly-YSZ layer (closed circle), a single (111)-YSZ substrate (cross), and a glass substrate (closed triangle) without preheating. Also, the $X_c$ of an Si
/poly-YSZ/glass with preheating (open circle) is shown. As a reference, the broken line indicates the $X_c$ of the Si film annealed at 700 °C for 30 min on a (111)-YSZ substrate. The $X_c$ of ~80% is considered to be an upper-limit value for our sample structures. At first, the non-preheating cases are mentioned. It can be seen that a retardation period or so-called incubation time $\tau_i$ before the beginning of the crystallization, and the crystallization rate $R_C = \Delta X_c/\Delta t_a$ of the Si/poly-YSZ/glass case are almost the same as those in the Si/(111)-YSZ case. Here, $\tau_i$ is defined by an intercepting time $t_a$ between the horizontal axis and the initial linear line of the crystalline fraction. The $\tau_i$ is also a kind of transition time which is necessary to detect a continuous crystallization phenomenon by Raman spectroscopy. Both of $X_c$s for Si on YSZ increase linearly with the annealing time $t_a$ as a whole. In contrast to this, the beginning of crystallization of the Si/glass is delayed by ~300 min and seems to increase non-linearly with $t_a$. From this result, we can consider the following growth model.

The location of nucleation may be at the interface, according to many other reports \(^{17,18}\), in which nucleation in an a-Si film occurs at the interface faster than in the bulk. But bulk nucleation cannot be excluded. Also, it is well known that, for bulk nucleation, an initial crystalline fraction varies as the fourth power of the annealing time, based on the assumptions that nucleation occurs randomly at a constant rate and that crystallization proceeds isotropically in direction and linearly in time. \(^{19}\) On the other hand, if the nucleation occurs at the interface uniformly like a sheet, the crystallization front would go straight toward the film surface linearly with the annealing time so that the $X_c$ should increase as well. This phenomenon has been already reported by other researchers. \(^{20,21}\) In the Si/poly-YSZ/glass and Si/(111)-YSZ cases, Si nucleation is induced at the YSZ interface, and Si-crystallized areas grown from the nucleation sites.
cover the YSZ interface more uniformly, compared with the Si/glass case. Later, we
discuss further this nucleation event. Then, the crystallization front progresses with time
linearly toward the film surface. On the contrary, in the Si/glass case, Si nucleation at
the interface of SiO₂ may occur non-uniformly in time and space more than in the
former cases. Although the initial nucleation site might not be in bulk, the possibility of
bulk nucleation increases with the annealing time. For example, at \( t_a \approx 1000 \) min, bulk
nucleation might occur so that the \( X_c \) increases rapidly with \( t_a \), as shown in Fig. 3.

The \( X_c \) saturation values in all of the cases are relatively low as a whole, and even
in the case of Si/(111)-YSZ, it is less than 80%. These smaller \( X_c \)s can be explained by
the dependence of the integrated Raman cross section \( \sigma \) on the grain size. The
related issue has been already discussed in our previous paper. The saturation value
decreases in the order of Si/(111)-YSZ, Si/poly-YSZ/glass, and Si/glass, which seems to
be due to the dependence on the crystallographic information quality of the underlying
substance. For example, the highest value for the Si/(111)-YSZ can be due to an almost
perfect information of single (111)-YSZ. However, for further discussion on this, we do
not have any clear evidence such as the crystallographic orientation, the grain size, and
the crystalline quality distribution in depth, expecting a preferential Si (111) orientation
on YSZ like the direct deposition case. Since it lies beyond the scope of this paper,
this will be discussed in future work in more detail.

The open circles in Fig. 3 indicate that preheating shortens \( \tau_i \) by \(-250 \) min as
compared to the non-preheating case of the Si/poly-YSZ/glass. This suggests that
thermal heating in the vacuum chamber should be effective to promote Si nucleation.
But the crystallization rate \( R_C = \Delta X_c / \Delta t_a \) is almost the same as in the non-preheating case,
which indicates that preheating hardly enhances \( R_C \). So, we should notice that no matter
how much the interface property is improved, $R_C$ is hardly changed although $\tau_i$ is shortened.

Figure 4 shows Arrhenius plots of the reciprocal of the incubation time $1/\tau_i$ of the three kinds of samples without preheating, the $1/\tau_i$ of Si/poly-YSZ/glass samples with preheating, and crystalline fraction rates $R_C$ of Si/(111)-YSZ and Si/poly-YSZ/glass samples without preheating, with respect to the reciprocal of the annealing temperature $T_A$. The solid and broken lines for the data of each sample group indicate calculation results by the least square method. The $R_C$ of the Si/glass sample is not shown because it is hardly determined due to the non-linear curve shown in Fig. 3. As one can see, each physical quantity exhibits the behavior of an activation process, and $1/\tau_i$ can be formulated by $C_i \exp(-E_i/kT)$, where $C_i$ and $E_i$ are a pre-exponential factor and an activation energy, respectively. The $E_i$s for the Si/(111)-YSZ, the Si/poly-YSZ/glass, and the Si/glass are estimated to be about 4.3, 4.0, and 3.9 eV, respectively. The activation energy $E_{ip}$ for Si/poly-YSZ/glass with preheating is about 3.4 eV, and the activation energies $E_C$ of $R_C$ for the Si/(111)-YSZ and the Si/poly-YSZ/glass are about 3.4 eV. The estimation error for them is less than 15% roughly. The $E_i$s of the three samples without preheating are similar within the error and are reduced by preheating. Also, the estimated $E_C$ is similar to the reported values of 3.1 to 3.4 eV.\(^{21, 24}\)

Here, we will discuss the results of Fig. 4. According to the previous review paper,\(^{24}\) it can be hypothesized that $1/\tau_i$ is proportional to a product of the nucleation site area density $S_n(T) = S_{n0} \exp(-E_S/kT)$ and the Si atomic jump frequency $\nu(T) = \nu_0 \exp(-E_v/kT)$ from amorphous phase to crystalline phase, as shown in the following eq. (1). $S_{n0}$ and $\nu_0$ are pre-exponential factors of $S_n(T)$ and $\nu(T)$, respectively, and $E_S$ and $E_v$ are activation energies of $S_n(T)$ and $\nu(T)$, respectively. So, $C_i$ and $E_i$ are
proportional to $S_{n0}$, $v_0$ and equal to $E_S + E_v$, respectively:

$$\tau_i = C_i \exp \left( - \frac{E_i}{kT} \right) \propto S_n(T) \nu(T) = S_{n0} \nu_0 \exp \left( - \frac{E_S + E_v}{kT} \right). \quad (1)$$

In the comparison between bulk nucleation (BN) and interface nucleation (IN), the $S_n$ of IN is larger than that of BN, since IN generally occurs more often, as mentioned before. Also, since $\nu$ depends mainly on the crystalline material, structure, and on the temperature, each $\nu$ for the three kinds of samples can be the almost same. Furthermore, it has been reported that, in the case of BN, $E_C$ is roughly equal to $E_i^{21,24}$ because both $E_C$ and $E_i$ strongly depend on Si atomic jumping between the amorphous-crystalline interface.

Based on these considerations, from the result of a $\tau_i$ of the Si/glass that is larger than that of the Si on YSZ, we can conclude that the former pre-exponential factor of $S_n$ is smaller than that of the latter because their $\nu$ are almost the same. Also, it seems reasonable that the $E_S$ of the three samples without preheating are roughly equal if it is hypothesized that the difference in $E_S$ is much smaller among the three samples, compared with $E_v$. Furthermore, we can explain the reason why, by preheating, the $E_i$ of the Si/poly-YSZ/glass is reduced to $E_{ip}$ and becomes close to the $E_C$ of the growth rate as follows: the interface of the YSZ without preheating has some contaminations or chemical unstable sites, which may easily react with Si to prevent Si movement. This may increase the $E_S$ of $S_n$. By preheating, the obstacles are roughly removed, so that the $E_S$ is reduced. Therefore, $E_i = E_S + E_v$ is reduced and the $E_{ip}$ becomes close to the $E_C$ of the crystallization growth rate.

There are still two questions concerning Figs. 3 and 4. The first one is that the $\tau_i$ for the Si/(111)-YSZ is almost equal to that for the Si/poly-YSZ/glass. It is supposed that the interface quality of the single (111)-YSZ must be much higher than that of the
poly-YSZ layer, so that the (111)-YSZ should have a shorter $\tau_i$ than the poly-YSZ. The second question is why the $S_n$ of Si on YSZ is larger than that for the Si/glass. To answer these questions, as a possible cause, we may think of the Zr and Y of the constituent elements of YSZ. From the concentration depth profiles of Zr and Y in the crystallized Si film on the poly-YSZ layer obtained by SIMS, where $t_a = 1320$ min and the preheating time = 60 min, it was found that Zr atoms diffuse into the crystallized film at a level of less than $1 \times 10^{18}$ atoms/cm$^3$, and that the Y signal is near $1 \times 10^{16}$ atoms/cm$^3$. From this result, this unignorable Zr concentration can be considered to be one possible factor for the larger $S_n$ irrespective of the interface crystalline quality. An interaction of the free electrons of Zr with the covalent electrons of a nearest neighbor Si might promote nucleation or bonding between Si atoms. On the other hand, it can be said that, for crystallization growth in the film bulk, the diffusion of Zr and Y is a negligible effect. This is not only because the SPC rate of about 50 nm/h shown in Fig. 2 is much lower than the MILC rates of more than 4 $\mu$m/h that is the popular reported value, but also because the impurity concentration level for Ni-MILC is greater than $\sim 0.08$ at% ($\sim 4 \times 10^{19}$ atoms/cm$^3$), which is much larger than in our case by 1.5 orders of magnitude. However, its effect on the electrical property for device application is to be taken into account so that we should investigate the electrical property of the crystallized Si film in future research.

In conclusion, we investigated the CI effect of YSZ in the solid phase crystallization of a-Si film by using three kinds of samples, which were a-Si film/poly-YSZ/glass, a-Si film/(111)-YSZ substrate, and a-Si film/glass. It was found that the $\tau_i$ of the poly-YSZ layer was shorter than that for the glass substrate, and was almost equal to that for the crystal (111) YSZ substrate. From the results of the Arrhenius plots of $1/\tau_i$, it was
deduced that the CI effect was not due to difference in \( E_i \) but to a higher \( S_n \) on YSZ, because the \( E_i \)'s of the three kinds of samples are similar. One possible factor for the higher \( S_n \) can be considered to be Zr, which is one component of YSZ. It was also found that the preheating prior to Si film deposition was effective in shortening \( \tau_i \). This is probably because the preheating reduces \( E_i \) from about 4.0 eV to about \( E_{ip} = 3.4 \) eV.
References


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Figure captions

Fig. 1 (Color online) Schematic diagrams of the three kinds of sample structures. (a) a-Si film deposited on a poly-YSZ film which covers the surface of a fused quartz substrate (Si/poly-YSZ/glass), (b) a-Si film deposited on a single crystal (111)-oriented YSZ substrate (Si/(111)-YSZ), and (c) a-Si film deposited on a fused quartz substrate (Si/glass).

Fig. 2 Raman spectra for the samples of the (a) Si/poly-YSZ/glass, (b) Si/(111)-YSZ, and (c) Si/glass. The annealing temperature $T_A$ is 560°C and the annealing time $t_a$ is a parameter.

Fig. 3 (Color online) Annealing time $t_a$ dependencies of the crystalline fractions $X_c$ of Si films deposited on a poly-YSZ layer (closed circle), a single (111)-YSZ substrate (cross), a glass substrate (closed triangle) without preheating, and on a preheated poly-YSZ layer (open circle). As a reference, the broken line indicates the $X_c$ of the Si film annealed at 700 °C for 30 min on a single (111)-YSZ substrate without preheating. The $R_C$ of the crystalline fraction rate is defined by $\Delta X_c/\Delta t_a$ of the initial slope of the linear line of the crystalline fraction versus $t_a$, and the $\tau_i$ of the incubation time is determined by the intercepting time $t_a$ between the horizontal axis and the linear line.

Fig. 4 (Color online) Arrhenius plots of the reciprocal of the incubation time $1/\tau_i$ and the crystalline fraction rates $R_C$ versus the reciprocal of the annealing temperature $T_A$. The solid and broken lines for the data of each sample group are calculated by the least
square method.
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Fig. 2
Fig. 3

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Fig. 4  

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