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Description	



1 **Low-Temperature Crystallization of Silicon Films Directly Deposited on Glass**
2 **Substrates Covered with Yttria-Stabilized Zirconia Layers**

3

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9 Si films were deposited at low temperatures on glass substrates covered with
10 poly-yttria-stabilized zirconia (YSZ) layers. We investigated the dependences of
11 crystallization on the Y content and cleaning solution for the YSZ layers. Transmission
12 electron microscopy showed that some regions of the Si film deposited at 430 °C were
13 directly crystallized on a YSZ layer without an amorphous region, where Si lattice fringes
14 were tightly connected to YSZ lattice fringes. The crystallization of Si films on YSZ layers
15 occurred at deposition temperatures lower than that on glass substrates by more than 100 °C.
16 Zr, Y, and F concentrations in the Si film were negligible, except the Zr concentration near
17 the interface. The discussion on the crystallization mechanism gave the following
18 suggestions on the method of obtaining a high crystalline fraction. The YSZ layer should be
19 chemically cleaned using a solution containing HF before Si film deposition, and the content
20 ratio $Y/(Zr+Y)$ of YSZ should be ≥ 0.2 .

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1 **1. Introduction**

2 Poly- or microcrystalline silicon (poly-Si) films fabricated at low temperatures are of
3 great interest for electron devices on temperature-sensitive and cheap substrates. A thin film
4 transistor (TFT) in an active matrix flat panel display is one of the appropriate applications of
5 the poly-Si films besides solar cells. Although hydrogenated amorphous silicon (a-Si:H)
6 TFTs are currently used in commercialized displays, their low carrier mobility of less than 1
7 $\text{cm}^2/(\text{V}\cdot\text{s})$ and their low reliability are the major drawbacks. Thus far, in order to obtain large
8 grains with high carrier mobility, solid phase crystallization (SPC),¹⁻³⁾ metal-induced
9 crystallization (MIC),⁴⁻⁷⁾ metal-induced lateral crystallization (MILC),⁸⁻¹¹⁾ and melting
10 crystallization by pulse laser annealing (PLA)¹²⁻¹⁴⁾ have been proposed, in which a-Si films
11 deposited on substrates are crystallized by annealing. The SPC method has the demerits of
12 high process temperature ($> 600\text{ }^\circ\text{C}$) and long annealing time ($> 12\text{ h}$). Although the MIC
13 method overcomes these issues on the SPC method, it also has a serious problem of metal
14 impurities, which are contained in crystallized films. The MILC method has been developed
15 in order to overcome this problem, but the impurity concentration is still higher than
16 $10^{18}/\text{cm}^3$.¹¹⁾ The PLA method has advantages over the other methods, such as low thermal
17 budget, large grain size, i.e., high mobility, and low impurity concentration. The equipment
18 cost, however, is high, and a crystallized Si film has large roughness and random grain
19 boundary location, which results in a low uniformity in device performance.¹⁵⁾ This is a
20 problem, especially for large-size and current-drive displays.

21 Uniformity in device parameters, e.g., mobility and threshold voltage, or in the
22 crystallinity of a poly-Si film over a large area is strongly required even though the grain size
23 is less than 50 nm and the mobility is low [$\sim 5\text{ cm}^2/(\text{V}\cdot\text{s})$]. As a possible method of fabricating
24 the desirable films, the direct deposition of poly-Si films has been investigated thus far by
25 using various methods of chemical vapor deposition (CVD)¹⁶⁻¹⁸⁾ and sputtering,^{19,20)} in which

1 poly-Si films can be obtained at deposition temperatures lower than 500 °C. In general,
2 poly-Si films deposited by these methods have columnar structures, and their grain sizes are
3 less than 50 nm. Furthermore, a thin amorphous transition layer or an incubation layer is
4 formed between the glass substrate and the polycrystalline region, and the crystallized films
5 are much defective.²¹⁻²⁴⁾ So, it has been reported often that the field effective mobilities of the
6 films are as low as or lower those of a-Si TFTs.^{24,25)}

7 Alternatively, the use of an induction layer for low-temperature crystallization
8 (crystallization-induction layer: CI layer) to cover an amorphous surface of a substrate has
9 been proposed.²⁶⁻²⁸⁾ The CI layer, which is a polycrystalline dielectric, should have similar
10 lattice constant and crystal structure to Si. The small lattice mismatch and same crystal
11 structure give some advantages for low-temperature crystallization, although the
12 heteroepitaxial growth of the Si film may not occur on the CI layer because of its too low
13 process temperature. First, on the basis of the crystallographic information of the CI layer,
14 the proposed method is considered to have the potential to reduce crystallization temperature,
15 compared with conventional direct deposition methods. Second, on the basis of the
16 crystallinity of the CI layer, it is possible to control the grain size and crystallographic
17 orientation of a deposited Si film. Therefore, the CI layer method can be expected to produce
18 poly-Si films at low temperatures in high mass production, and the films have a high
19 uniformity in crystallinity as well as low impurity concentration and small surface roughness.
20 It should be, however, noted that enlargement of grain size by this method is unpromising
21 because of the direct deposition of the polycrystalline film.

22 As CI materials, ZrO₂²⁶⁾ and CaF₂^{27,28)} have been proposed thus far. However, on the
23 ZrO₂ layer, an amorphous incubation layer is formed, which means that ZrO₂ does not act as
24 an actual CI material. CaF₂ is not an appropriate candidate material for electron devices
25 owing to its low breakdown voltage and fluoride trap charges. On the other hand, our group

1 used a polycrystalline yttria-stabilized zirconia ($(\text{ZrO}_2)_{1-x}(\text{Y}_2\text{O}_3)_x$: YSZ) layer.²⁹⁾ It has been
2 reported that YSZ films can be grown heteroepitaxially at temperatures higher than 800 °C
3 on Si and vice versa^{30,31)} because of the small lattice mismatch of ~ 5% with Si and the same
4 cubic crystal structure. We have reported that Si films deposited on YSZ layers were
5 crystallized, while Si films on glass substrates were still amorphous at the deposition
6 temperature $T_S = 430$ °C.³²⁾ It was also found that the chemical cleaning of the surface of a
7 YSZ layer just prior to Si film deposition is a critical key process. After dipping YSZ layers
8 into HF solution for removing contaminated and damaged surface layers, they were rinsed
9 with ethanol solution or deionized water (DIW). The Si films deposited on the ethanol-rinsed
10 YSZ layers were crystallized, but not those on the deionized-water (DIW)-rinsed YSZ layers.
11 The following reason was proposed. During the HF etching process, F atoms adsorb on the
12 YSZ layer surface. Even after the ethanol rinsing process, some of the F atoms remain on the
13 layer surface, and the residual F atoms may protect the bare etched YSZ surface from
14 exposure to contaminants in the preparation atmosphere. Just before Si film deposition in a
15 vacuum chamber, most of the F atoms desorb at substrate heating. Therefore, the residual F
16 atoms can contribute to the smooth transmission of crystallographic information from the
17 YSZ surface to the deposited Si. Because the residual amount of F atoms after the DIW
18 rinsing process was much smaller than that after the ethanol rinsing process, Si
19 crystallization on the DIW-rinsed YSZ layers hardly occurred.

20 Recently, we have found that crystalline fractions of Si films were strongly dependent
21 of the yttrium content ratios $R_{\text{YA}} = \text{Y}/(\text{Zr}+\text{Y})$ of as-deposited YSZ layers. R_{YA} in the previous
22 report was less than 0.1.³²⁾ However, when R_{YA} was 0.21, even on DIW-rinsed YSZ layers,
23 the crystallization of Si films occurred at 430 °C.³³⁾ In this paper, we show the inclusive
24 investigation results of the Y content ratio dependence of Si film crystallization from $R_{\text{YA}} =$
25 0.02 to 0.3 as well as the rinse solution dependence, and discuss the crystallization

1 mechanism. Furthermore, we report on the distributions of the impurities Zr, Y, F, and O in
2 the crystallized Si film and the deposition temperature dependence of Si crystalline fraction.

3

4 **2. Experimental**

5 The substrate was a $2 \times 1 \text{ cm}^2$ fused quartz plate covered with a 70-nm-thick
6 polycrystalline (111) YSZ layer, which was deposited by reactive magnetron sputtering with
7 an Ar + O₂ mixture gas. The sputtering target was a Zr metal target, on which 8 pieces of 1×1
8 cm^2 Y were placed in a circular arrangement. The details were mentioned elsewhere.³⁴⁾

9 Before the deposition of an Si film, the YSZ layer was dipped in a diluted 5% HF solution for
10 3 min to remove the contaminated and damaged surface layer. The HF-dipped YSZ layer was
11 rinsed with ethanol solution or DIW just before being loaded into a deposition chamber. We
12 deposited an a-Si film on the YSZ/quartz substrate by electron beam evaporation at a
13 deposition temperature T_S of 300 to 550 °C with a deposition rate of 1 nm/min in $\sim 10^{-6}$ Pa.
14 The film thickness was mainly 60 nm, otherwise it will be mentioned. The crystallization
15 fractions of the Si films were characterized by Raman spectroscopy using an excitation light
16 of a 632.8 nm HeNe laser beam with a diameter of about 1 μm . The obtained Raman spectra
17 were decomposed into the following three components: a crystalline component peak at
18 $515\text{--}520 \text{ cm}^{-1}$, an amorphous component peak at around 480 cm^{-1} , and an intermediate
19 component peak at $500 \sim 510 \text{ cm}^{-1}$, which is associated with bond dilation at grain
20 boundaries. As an indication of crystalline fraction, we used a calculated value of the
21 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
22 intensities corresponding to the crystalline, intermediate, and amorphous component peaks,
23 respectively, and σ is the ratio of the integrated Raman cross section for amorphous phase to
24 crystalline phase. In this study, σ was chosen to be 1 for simplicity,³⁵⁻³⁷⁾ although it depends
25 on the grain size and the energy of the excitation beam.^{38,39)} The microstructures of the Si

1 films were observed by transmission electron microscopy (TEM). The surface crystallinity of
2 some samples was observed by *in situ* reflected high-energy electron diffraction (RHEED)
3 during the Si film depositions. The chemical states of the YSZ surfaces were evaluated by
4 X-ray photoelectron spectroscopy (XPS) using Al K α (1486.6 eV) as an X-ray source and the
5 take-off angle $\theta = 35^\circ$. The binding energies (BEs) were calibrated using an adventitious
6 carbon peak C 1s (284.6 eV) as a standard reference. In order to inhibit surface charging
7 effects, a low-energy electron flood gun was used.^{40,41)} The Y content ratio of the YSZ layer
8 was estimated from the integrated intensities of the Y 3d and Zr 3d peaks of XPS spectra,
9 which were normalized by the atomic sensitivity factors. The estimation error was roughly
10 determined to be $\pm 10\%$. In this paper, we define yttrium ratio after chemical treatment as
11 R_{YC} , since the chemical composition of the chemically treated YSZ surface was generally
12 changed from that of the as-deposited YSZ surface, R_{YA} . Depth profiles of Zr, Y, F, and O in
13 the deposited Si films were measured by secondary ion mass spectrometry (SIMS) in order to
14 investigate the diffusion of impurities in 60 and 120-nm-thick Si films during the deposition.

15

16 **3. Results**

17 Figure 1 shows the Raman spectra of the Si films deposited on the YSZ layers and glass
18 substrates, where (a) and (b) are for the ethanol-rinse and the DIW-rinse cases, respectively.
19 The R_{YA} values for the ethanol-rinse case are 0.02 and 0.16, and those for the DIW-rinse case
20 are 0.08 and 0.21. In each of the Si films on the glass substrates in both figures, we observe a
21 broad and large peak around 480 cm^{-1} due to an a-Si phase. In Fig. 1(a) for the ethanol-rinse
22 case, the spectra on the YSZ layers show sharp peaks at 518 cm^{-1} due to a crystalline silicon
23 (c-Si) phase regardless of R_{YA} , where the intensity for the high $R_{YA} = 0.16$ is much larger than
24 that for the low $R_{YA} = 0.02$. In Fig. 1(b) for the DIW-rinse case, however, the spectrum for
25 the high $R_{YA} = 0.21$ shows a strong crystalline peak, and that for the low $R_{YA} = 0.08$ shows a

1 broad amorphous peak. The result in Fig. 1 suggests that both the types of rinse solution and
2 Y content markedly influence the crystallization of the deposited Si films.

3 Figure 2 shows the dependence of Y content on the crystalline fraction X_C of the Si
4 film. Squares and triangles indicate data for the ethanol-rinse and DIW-rinse cases,
5 respectively. These symbols present the averages of 3 to 5 measurement points of one sample,
6 and the top and bottom error bars indicate the maximum and minimum values, respectively.
7 It can be seen that, in the low Y content region below $R_{YA} = 0.10$, the Si films on the
8 ethanol-rinsed YSZ layers are crystallized, but those on the DIW-rinsed YSZ layers are fully
9 amorphous. Furthermore, the X_C values for the ethanol-rinse case markedly fluctuate, which
10 means that the degree of crystallization is not uniform on the entire YSZ layer even under the
11 same deposition conditions of the Si films. Near $R_{YA} = 0.10$, the Si films deposited on the
12 DIW-rinsed YSZ layers are crystallized slightly. The X_C values for both the ethanol- and
13 DIW-rinse cases increase with Y content and become almost saturated around 50% when R_{YA}
14 > 0.20 . It can be concluded that, in the low Y content region, the ethanol rinsing process is
15 more effective in inducing Si crystallization than the DIW rinsing process. The detailed
16 mechanism will be discussed later.

17 The c-Si peak positions of the Raman spectra for the samples in Fig. 2 were
18 independent of R_{YA} and within the range from 518 to 519 cm^{-1} , which is lower than 520 cm^{-1}
19 for bulk c-Si. This means that the deposited Si films experience tensile stress.^{42,43)} The tensile
20 stress of the deposited Si films is mainly caused by the difference between the thermal
21 expansion coefficients of Si and glass, which are 2.8×10^{-6} and $0.5 \times 10^{-6} / ^\circ\text{C}$, respectively. The
22 full-widths at half-maximum (FWHMs) of the peaks ranged from 6.5 to 7.5 cm^{-1} . These
23 values were larger than 4.7 cm^{-1} for the measured bulk Si and 5.5 to 6.5 cm^{-1} for poly-Si
24 films by PLA;⁴⁴⁾ however, they were much smaller than the reported microcrystallite values
25 of more than 10 cm^{-1} .⁴⁵⁾ It has been reported that FWHM is strongly related to crystalline

1 defect density, i.e., a small FWHM for a small defect density.^{44,46)} Therefore, this strong
2 relationship indicates that the crystallized Si films produced by the CI method have higher
3 defect densities than those produced by the PLA method; however, such defect densities are
4 much smaller than those of microcrystallites.

5 We also monitored the *in situ* growth of the deposited Si film by RHEED. Figure 3
6 shows the (a) RHEED pattern of the bare YSZ layer at 430 °C and (b)–(d) those of the Si
7 films deposited on the DIW-rinsed YSZ layers with $R_{YA} = 0.13$ at $T_S = 430$ °C in order of
8 sequential deposition time. As a reference, a halo pattern of an amorphous Si (a-Si) film is
9 also shown in Fig. 3(e). In Fig. 3(a), a spotty pattern is observed. Since the pattern from the
10 YSZ layer was the same as that for any incident e-beam direction, it was found that the YSZ
11 layer had a fiber texture or a preferential orientation of (111), which was in good agreement
12 with the result of the XRD measurement. From the initial stage [Fig. 3(b)] to the final stage
13 [Fig. 3(d)] of Si film deposition, the spot patterns can still be observed; however, they are
14 more diffused than those in Fig. 3(a). From this result, it can be inferred that the
15 crystallization of the Si film partially occurred on the DIW-rinsed YSZ layer during the
16 deposition.

17 Figures 4(a) and 4(b), respectively, show the cross-sectional low-resolution and
18 high-resolution (HR-) TEM images of the Si film deposited at $T_S = 430$ °C on the
19 DIW-rinsed YSZ layer with $R_{YA} = 0.21$. The HR-TEM image in Fig. 3(b) shows a close-up
20 image of one area around the interface, which is enclosed by a dotted frame in Fig. 4(a). This
21 also shows the electron-diffraction (ED) patterns simulated by using the fast Fourier
22 transform (FFT) based on the local lattice images enclosed by white and black square frames
23 labeled as point 1 and point 2, respectively. Some large regions of the Si film grow directly
24 from the YSZ layer without an amorphous transition region, although the other regions, e.g.,
25 point 3, are in the amorphous phase. For example, at the Si/YSZ interface of point 4, the start

1 points of the lattice fringe lines of the crystallized Si film coincide with the end points of the
2 YSZ layer one by one. The strong spots in both the ED patterns correspond to $\{111\}$ planes,
3 except for the two spots of YSZ $\{200\}$ indicated by white arrows. From these patterns, the
4 crystallographic orientation normal to the interface can be identified as $\langle 111 \rangle$, which is the
5 preferential orientation of the YSZ layer. Both the ED patterns also show a $\{110\}$ plane,
6 although they are rotated by 180° along the axis normal to the interface or $\langle 111 \rangle$. This
7 suggests that the crystallites of points 1 and 2 have a twinlike crystallographic relationship
8 despite of heteromaterials. It has been well known that microtwins easily form in Si films
9 grown epitaxially on Si(111) substrates⁴⁷⁻⁵⁰⁾ and in poly-Si films grown by SPC.⁵¹⁾ It has also
10 been reported that when the interface between the amorphous and crystalline phases is rough,
11 microtwins are observed well often.⁴⁷⁾ Thus, the twinlike relationship in our case may also be
12 due to the roughness of the interface, as shown in Fig. 4. From this result, it can be
13 considered that the nucleation was stimulated by the crystallographic information of the YSZ
14 layer, from where the crystallization of the upper amorphous region occurred and progressed
15 up to the surface. However, the crystallized Si regions contain many defects, e.g., twins and
16 dislocations. The amorphous regions also exist in the Si film. We speculate the reason why
17 mixture of amorphous and crystalline phases exists in the vicinity of the interface as follows:
18 Just before the Si film deposition, the YSZ surface condition is not controlled perfectly and is
19 not uniform over the entire area owing to grain boundaries, unremoved contaminants,
20 microroughness, and so on. The X_C at $R_{AY} = 0.2$ in Fig. 2 is about 40%, which is small
21 compared with that in the TEM images shown in Fig. 4, even though the errors in Raman
22 measurement and its analysis are about 10%. The main reason for this is the assumption that
23 the ratio of the integrated Raman cross section σ is set to be 1 for simple calculation.
24 According to Bustarret et al.'s report,³⁸⁾ σ can be expressed experimentally as $\sigma = 0.1 +$
25 $\exp(-L/10)$ for a wavelength of 632.8 nm, where L is the grain size in nm. Using this equation,

1 the corrected crystalline fraction for $X_C = 40\%$ is calculated to be about 74% when the
2 average grain size is $L = 20$ nm, taking the TEM images in Fig. 4 and the FWHM of the
3 Raman spectra in Fig. 1 into account. This value seems to be reasonable for the TEM images.

4 Next, we observed XPS spectra from surfaces of YSZ layers. They can give us important
5 information on the chemical bond states of the YSZ components from the viewpoint of the
6 crystallization of the Si films deposited on the YSZ layers. Figure 5 shows the XPS spectra
7 from the (i) as-deposited, (ii) HF-dipped, and (iii) DIW-rinsed YSZ layers with $R_{YA} = 0.13$. In
8 this figure, two notable points are observed. One is the ratio of the yttrium Y 3d peak intensity
9 to the zirconium Zr 3d peak intensity, and the other is the F 1s peak intensity due to F atoms
10 adsorbed on the YSZ surface. The calculated Y content ratio of the HF-dipped YSZ layer was
11 determined to be 0.33, which is much larger than the as-deposited YSZ layer $R_{YA} = 0.13$.
12 However, after the DIW rinsing process, the Y content ratio becomes almost the same as the
13 as-deposited YSZ layer value. In other words, both Y and Zr atoms are etched by HF dipping,
14 but certain amounts of the etched and dissolved Y atoms adsorb on the YSZ layer surface.
15 Most of them, however, are removed by DIW rinsing. The DIW rinsing process also removes
16 the adsorbed F atoms, leaving a small amount of them. If Zr atoms are etched selectively by
17 the HF solution and Y atoms are bonded to O atoms constructing the YSZ layer, the Y
18 content ratio after the DIW rinsing process will be much higher than R_{YA} and will be near the
19 value obtained after the HF dipping process.

20 Figure 6(a) shows the R_{YA} dependences of the Y content ratios of the chemically treated
21 YSZ layers (R_{YC}), namely the HF-dipped layers without rinsing (circles), ethanol-rinsed
22 layers (squares), and DIW-rinsed layers (triangles). It can be seen from this figure that the
23 R_{YC} values of all the samples increase with R_{YA} . The R_{YC} values of the ethanol-rinsed layers
24 are almost equal to those of the HF-dipped layers, and roughly twice larger than R_{YA} . The
25 incremental Y ratio $\Delta R_{YC} = R_{YC} - R_{YA}$ is due to the adsorption of dissolved Y atoms in the

1 HF solution, as mentioned previously. In contrast, the R_{YC} of the DIW-rinsed YSZ layer is the
2 lowest among the three treatments, being roughly proportional to R_{YA} , as indicated by the
3 solid line $R_{YA} = R_{YC}$. However, for a high $R_{YA} \gtrsim 0.15$, R_{YC} has a slightly larger $\Delta R_{YC} \approx 0.05$
4 than R_{YA} . Figure 6(b) shows the relationship between R_{YA} and R_F , where R_F is the F ratio to
5 $Zr+Y$, $F/(Zr+Y)$, for the same chemically treated YSZ layers as those in Fig. 6(a). The R_F of
6 any treated YSZ layer increases with R_{YA} , and the R_F of the DIW-rinsed layers is the lowest
7 among the three treatments. The highest R_F is obtained from the as-HF-dipped layers,
8 followed by that obtained from the ethanol-rinsed layers. It can be seen that 60–80% of the
9 amount of adsorbed F atoms remains after the ethanol rinsing process, but only 25–35% of
10 the amount of adsorbed F atoms remains after the DIW rinsing process. Furthermore, the R_F
11 values for the two rinse solutions become saturated with increasing R_{YA} over 0.15. The
12 saturation level of R_F for the ethanol-rinse case is ~ 1.0 , which is twice that (~ 0.5) for the
13 DIW-rinse case. Comparing Fig. 6(a) with Fig. 6(b), it seems that there is a relationship
14 between the amounts of adsorbed Y and F atoms on the YSZ layers after the rinsing process.
15 These phenomena will be discussed in detail later.

16 Figures 7(a) and 7(b) show the concentration depth profiles of Zr and Y, and O and F,
17 respectively, in the 120-nm-thick Si film deposited on the ethanol-rinsed YSZ layer at 430 °C,
18 where X_C was $\sim 45\%$ and R_{YA} was ~ 0.16 . Figure 7(c) shows the concentration depth profiles
19 of O and F in the 60-nm-thick Si film deposited on the DIW-rinsed YSZ layer at 430 °C. In
20 this case, the Si film was amorphous because R_{YA} was low (~ 0.08), as shown in Fig. 2. Since
21 the quantitative concentrations were estimated by using a standard sample of an
22 ion-implanted amorphous Si, the concentrations in the Si film are valid in this figure. The
23 concentrations near the interface and in the YSZ layer are incorrect because of the so-called
24 matrix and charge-up effects due to the insulator of YSZ.⁵²⁾ From Fig. 7(a), it can be seen that
25 Zr atoms diffuse into the crystallized film slightly. The Zr concentration at the Si/YSZ

1 interface is about 5×10^{18} atoms/cm³ and decreases towards the surface of the Si film below
2 the background level of 2×10^{16} atoms/cm³. It has been reported that Zr atoms from the ZrO₂
3 film hardly diffuse into Si even at 700 °C for 5 min for the application of a gate insulator.⁵³⁾
4 In our case, a certain amount of chemically unstable Zr due to HF dipping might remain on
5 the YSZ surface before the Si film deposition; however, a clear reason for this is not found at
6 present. Unlike Zr, the Y signal is below the background level, thus, Y can be a negligible
7 impurity in the Si film. Although the Zr and Y concentrations for the DIW-rinse case are not
8 shown here, they are considered to be the same as those in Fig. 7(a) because there is no
9 essential difference between the two processes with respect to diffusion. From this result, we
10 can consider that the diffusion of Zr and Y into the deposited Si film from the YSZ layer is
11 negligible, except in the vicinity of the interface. We should further suppress the diffusion of
12 Zr near the interface for device application.

13 In Fig. 7(b), it can be seen that the O and F concentrations for the ethanol-rinse case are
14 on the orders of 1×10^{18} and 1×10^{17} atoms/cm³, respectively, in the bulk of the Si film.
15 Although the O concentration is negligible for device performance, the F concentration
16 seems relatively higher. In contrast, in Fig. 7(c) for the DIW-rinse case, the F concentration is
17 less than 1×10^{16} atoms/cm³ in the bulk of the Si film and much smaller than that in Fig. 7(b).
18 This concentration as well as the O concentration is acceptable for obtaining a high device
19 quality. The two reasons for the lower F concentration for the DIW-rinse case can be
20 considered to be 1) the higher rinsing effect for removing the residual adsorbed F atoms and
21 2) the evaporation of F atoms from the YSZ layer by heating at $T_s = 430$ °C in the vacuum
22 chamber. For the ethanol-rinse case, a certain amount of adsorbed F atoms remains even after
23 substrate heating, as indicated in the previous report.³²⁾ In both Figs. 7(b) and 7(c), the O and
24 F concentrations increase toward the surface of the Si film. Probably, O atoms adsorbed on
25 the Si film from the atmosphere and then diffused into the film. F atoms also probably

1 adsorbed on the Si film chemically cleaned by using the HF solution to remove the native
2 oxide before the SIMS measurement. However, even after the DIW rinsing process, a small
3 amount of adsorbed F atoms might remain on the Si film.

4 The deposition temperature T_S dependences of the crystalline fractions X_C for the
5 ethanol-rinse cases are shown in Fig. 8. Closed squares and open squares indicate the data for
6 the Si films deposited on the YSZ layers with $R_{YA} \geq 0.13$ and on the glass substrates without
7 a YSZ layer, respectively. It can be seen that, at $T_S < 400$ °C, the Si films deposited on the
8 glass substrates are fully amorphous, but those on the YSZ layers are partially crystallized.
9 By increasing the T_S to 430 °C, the Si film on the glass substrate starts crystallizing. The X_C
10 values of both films increase with T_S and tend to saturate at ~60% at temperatures above 500
11 °C. From this result, it can be considered that the nucleation rate of Si is strongly dependent
12 of the interface material, but the saturation level of X_C is almost independent of it. Actually,
13 at $T_S > 500$ °C, the CI layer effect of YSZ may become negligible. This is probably because a
14 higher T_S or a higher thermal energy enhances more the surface migration of the deposited
15 Si; thus, the Si film is crystallized without the effect of the interface material. Therefore, it is
16 supposed that, above $T_S = 500$ °C, the same crystalline quality of the initial Si layers on the
17 YSZ layer and glass substrate leads to the same crystalline fraction of X_C , as shown in Fig. 8.
18 Although the T_S dependence of X_C has not been investigated for the DIW-rinsed YSZ layer,
19 the tendency will almost be the same as that in Fig. 8, provided that $R_{YA} \geq 0.2$.

20 Figures 9(a)–9(c) show the surfaces of the Si films deposited at $T_S = 320, 350,$ and 430
21 °C, respectively, on the ethanol-rinsed YSZ layers, which were observed by SEM. The Si
22 films were Secco-etched to delineate grain boundaries before the observation. The arrow in
23 Fig. 9(c) indicates a hole formed by Secco-etching a local amorphous region. The X_C values
24 for $T_S = 320, 350,$ and 430 °C are 1.5, 18, and 37%, respectively. In this figure, the
25 crystallized grains are observed on the etched Si film deposited even at 320 °C. This means

1 that the critical deposition temperature for crystallization on the YSZ layer is as low as 320
2 °C, which is in good agreement with that in Fig. 8. It can also be seen that the Si grain
3 density increases with T_S , although the uniformity of grain size is reduced with it. This is
4 probably because the nucleation rate increases with T_S . According to the result in Fig. 4, it
5 can be inferred that the nucleation sites locate on the YSZ layer, and that the growth front
6 proceeds not only upward in height but also laterally in width during the deposition. When
7 the deposition temperature is 320 °C, the nucleation density on the YSZ layer is so low that
8 the distance between the nucleation sites (DN) may be larger than the final size of the grain.
9 Therefore, since the grains can be grown without collision with one another up to the final
10 deposition thickness, they are similar in size. When the deposition temperature is set higher,
11 e.g., $T_S = 430$ °C, the nucleation density increases such that some lateral growth fronts of
12 grains may impinge with one another randomly during the deposition. As a result, the
13 distribution of grain size becomes nonuniform compared with those in the lower T_S cases as
14 shown in Fig. 9(c). In the future, we should investigate the relationship between the YSZ and
15 crystallized Si grains in terms of size and orientation.

16

17 **4. Discussion**

18 In this section, we discuss the crystallization mechanism of the Si films deposited on
19 the chemically treated YSZ layers at the low temperature of 430 °C. Under this condition, the
20 Si films deposited directly on the glass substrates are amorphous. Particularly, we focus on
21 the dependence of the crystalline fraction on the as-deposited Y content ratio R_{YA} , as shown
22 in Fig. 2. From Figs. 2 and 6(b), it can be seen that, for the DIW-rinse case, when R_{YA}
23 decreases from 0.15 to less than 0.08, the crystalline fractions X_C markedly decrease from
24 about 30% to zero, although the F ratios R_F decrease slightly. On the other hand, as
25 mentioned in the previous report,³⁴⁾ R_{YA} affects the crystal structure and crystalline quality of

1 YSZ layers. At a very low $R_{YA} \leq 0.02$, YSZ films are in monoclinic phase with a low
2 crystalline quality. As R_{YA} increases, crystal structures transform to a more stable tetragonal
3 phase with a higher crystalline quality, followed by a cubic phase. From these results, it is
4 supposed that important factors for the low-temperature crystallization of Si films are not
5 only surface protection due to F atoms adsorbed on the YSZ layers but also the YSZ surface
6 crystalline quality.

7 Figure 10(a) shows the two narrow scan XPS spectra of Zr 3d from the DIW-rinsed YSZ
8 layers with the high $R_{YA} = 0.21$ and low $R_{YA} = 0.07$, compared with the spectrum from the
9 as-deposited YSZ layer with the high $R_{YA} = 0.21$. The RHEED pattern is also shown, which is
10 mentioned later. The shapes of the Zr 3d peaks from both the DIW-rinsed YSZ layers are
11 similar to that from the as-deposited YSZ layer. The shape of the Zr 3d peak from the
12 HF-dipped YSZ layer, not shown here, is also almost the same as that from the as-deposited
13 YSZ layer. These results mean that the chemical state of surface Zr within the escape depth
14 of ~ 2 nm⁵⁵⁾ is hardly changed by the cleaning processes. However, the peak of the low R_{YA} is
15 shifted to an energy higher than that of the high R_{YA} by ~ 0.5 eV because of a chemical shift
16 caused by increasing yttrium content.⁵⁵⁾ Figure 10(b) shows the three narrow-scan XPS
17 spectra of Y 3d from the DIW-rinsed YSZ layers with the high $R_{YA} = 0.21$ and low $R_{YA} = 0.07$,
18 and from the ethanol-rinsed YSZ layer with the low $R_{YA} = 0.06$. As a reference, the spectrum
19 from the as-deposited YSZ layer with the high $R_{YA} = 0.21$ is also shown. The Y 3d signals are
20 split into the two peaks or doublets, $3d_{5/2}$ and $3d_{3/2}$, due to spin-orbit coupling, which holds
21 true for Zr 3d, as shown in Fig. 10(a). The arrows in the figure indicate the literature values
22 of binding energies (BEs) of Y_2O_3 ,^{54,55)} yttrium-bonded with a hydroxide Y-OH,⁵⁵⁾ and
23 YF_3 .^{54,56,57)} It can be seen in this figure that the shape from the DIW-rinsed YSZ layer with
24 the high $R_{YA} = 0.21$ is similar to that from the as-deposited YSZ layer. However, the shapes of
25 the other two spectra from the low $R_{YA} = 0.07$ and 0.06 are much different from them and

1 apparently broader. The spectrum from the DIW-rinsed YSZ layer with the low $R_{YA} = 0.07$
2 has some high-BE subcomponents, such as Y-OH and YF_3 , as well as a main component,
3 which is Y_2O_3 . The spectrum from the ethanol-rinsed YSZ layer with the low $R_{YA} = 0.06$ also
4 shows the same subcomponents. In this case, particularly, the YF_3 component at around 160
5 eV is very strong, as reported previously.³²⁾ Furthermore, it seems that the two spectra from
6 the DIW-rinsed layers also overlap slightly with small signals due to YF_3 . The result
7 indicating that F ions preferentially bond to Y ions over Zr ions coincides with the following
8 reports. When YSZ is dipped into HF solution, Zr is solved as an anionic fluoride complex
9 ion, such as $[ZrF_6]^{2-}$.⁵⁸⁾ As for Y, it has been reported that, although Y is also solved, insoluble
10 YF_3 is formed on the surface of YSZ in the HF solution.⁵⁹⁾ Thus, we observe Y bonded to F
11 in the XPS spectra of YF_3 .

12 It was observed that the shape of Y 3d from the HF-dipped YSZ layer was similar to that
13 from the ethanol-rinsed YSZ layer. According to this result and the result shown in Fig. 6(a),
14 where the R_{YC} of the ethanol-rinsed layer is almost equal to that of the HF-dipped YSZ layer,
15 it can be considered that Y atoms bonded to F atoms are hardly removed by ethanol rinsing.
16 However, as shown in Fig. 6(b), a certain amount of F atoms adsorbed on the HF-dipped
17 YSZ layer is removed by ethanol rinsing. The removed F may be bonded to other positive
18 ions, except Y ions. Therefore, it can be considered that ethanol rinsing process hardly
19 removes YF_3 molecules adsorbed on the HF-dipped YSZ layer. Furthermore, the DIW rinsing
20 process can wash away more F atoms as well as Y atoms bonded to F, but not completely.
21 This is probably because the dielectric constant ϵ of water (~ 78) at room temperature (RT) is
22 much higher than ~ 25 for ethanol at RT. The higher ϵ reduces the ionic bond strength due to
23 Coulomb force. Thus, the ethanol rinsing process can hardly wash away F atoms bonded to Y
24 atoms, but it can remove F atoms bonded weakly to other ions. In contrast, the DIW rising
25 process can easily remove F atoms bonded to Y atoms. However, the removal of F atoms is

1 partial and a certain amount of F atoms still remains on the YSZ layer, as shown in Fig. 6(b).
2 Owing to a slightly higher shoulder peak intensity at around 159 eV in Fig. 10(b), it is
3 supposed that the remaining F atoms are partially bonded to Y atoms even after the DIW
4 rinsing process.

5 On the other hand, Fig. 10 also shows the RHEED pattern of the DIW-rinsed YSZ
6 layer with the low $R_{YA} = 0.07$ at 430 °C just before the Si film deposition. This pattern is
7 more diffused than the pattern of the high R_{YA} [Fig. 3(a)]. This indicates that the surface
8 crystalline quality with the low R_{YA} is lower than that with the high R_{YA} . According to the
9 XPS spectra and RHEED pattern in Fig. 10, we can speculate as follows: The low quality
10 YSZ surface with the low R_{YA} may be much chemically active. If there is no sufficient
11 amount of F atoms to cover the entire YSZ surface, which may occur at a small R_F , the
12 chemically active sites may enhance the direct adsorption of contaminants on the YSZ layer
13 from the experimental environment. As well known,⁶⁰⁻⁶²⁾ the contaminants are probably
14 hydrocarbon, oxidized carbon and/or oxidized hydrocarbon adsorbed on the chemically
15 treated surface. These contaminants are not only from the laboratory room but also from the
16 vacuum chamber. In fact, signals due to C were inevitably observed in the XPS spectra from
17 the YSZ layers in our work.

18 On the basis of the above-mentioned experimental results and discussion, we consider a
19 comprehensive mechanism for the Si film crystallization using the schematic diagrams in Fig.
20 11. The surface of the as-deposited YSZ layer is damaged by highly energetic particle
21 bombardment during sputtering deposition and contaminated by exposure to the atmosphere.
22 The damaged and contaminated layer is removed or etched by HF dipping, which provides
23 crystallographic ordered sites at the surface. Simultaneously, a large amount of F atoms, as
24 well as etched and dissolved Y atoms, are adsorbed on the surface. Furthermore, as
25 mentioned in Fig. 6, the amounts of adsorbed Y (R_{YC}) and F (R_F) atoms increase with R_{YA}

1 owing to the HF dipping process. After the ethanol rinsing process, F atoms bonded to Y
2 atoms remain as YF_3 molecules on the YSZ surface and some F atoms without Y are
3 removed since the R_{YC} and XPS spectrum of Y are almost the same as those of the HF-dipped
4 YSZ layer. On the other hand, although the DIW rinsing process removes larger amounts of
5 adsorbed F and Y atoms, certain amounts of adsorbed F and Y atoms still remain on the YSZ
6 layer. In particular, for a high $R_{YA} \gtrsim 0.15$ ($\Delta R_{YC} \approx 0.05$), R_F becomes saturated at ~ 0.5 .

7 Because the saturation of R_F is an important phenomenon for the low-temperature
8 crystallization of the Si film, we discuss it in more detail using a model as follows: It is
9 speculated that, after the DIW rinsing process, the surface of the YSZ layer with $R_{YA} \gtrsim 0.2$
10 is covered almost fully with one monolayer consisting of F+Y ions. The excess F+Y ions
11 over one monolayer, which are generated by HF dipping, are removed by DIW rinsing. The
12 ethanol rinsing process may leave about two F+Y monolayers since R_F after the ethanol
13 rinsing process is about twice that after the DIW rinsing process, as shown in Fig. 6(b). The
14 lower and upper monolayers on the ethanol-rinsed YSZ layer might be bound through
15 Coulomb attractive interaction among the constructing ions. However, this interaction is not
16 so strong that the upper layer can be removed by rinsing with DIW whose dielectric constant
17 is much larger than the ethanol one. Some F ions in the F+Y monolayer on the DIW-rinsed
18 YSZ layer are bonded to Y ions constructing the surface of the YSZ layer. Since one of the
19 three bonds of Y^{3+} ion must be bound to one O^{2-} ion in the YSZ layer, the other two bonds
20 are bound to the two F^- ions in the monolayer. This is similar to O-Y-F₂. On the other hand,
21 Y^{3+} ions in the monolayer, which corresponds to $\Delta R_{YC} \approx 0.05$, are bound to three F^- ions to
22 form YF_3 . Since the Coulomb interaction between the F+Y monolayer and the YSZ layer
23 may be strong, the DIW rinsing process is supposed to hardly remove the monolayer.

24 Using the above-mentioned model, we estimate the area densities of Y^{3+} ions bonded
25 with three F^- ions in the monolayer, σ_{Ym} , and Y^{3+} ions bonded with two F^- ions and one O^{2-}

1 ion, σ_{YF} . The area density of total F^- ions is defined as $\sigma_{\text{F}} = 3\sigma_{\text{Ym}} + 2\sigma_{\text{YF}}$. Using $R_{\text{YC}} \approx 0.25$
2 at $R_{\text{YA}} \approx 0.2$, take-off angle $\theta = 35^\circ$, YSZ lattice constant $a = 0.514 \text{ nm}$,⁶³⁾ F^- ion radius $r_{\text{F}} =$
3 0.133 nm ,⁶⁴⁾ and the escape depth of Zr 3d and Y 3d photoelectrons $\lambda = 2 \text{ nm}$,⁵⁵⁾ we can
4 calculate $\sigma_{\text{mY}} = 1.95 \text{ nm}^{-2}$, $\sigma_{\text{YF}} = 3.03 \text{ nm}^{-2}$, and $\sigma_{\text{F}} = 11.91 \text{ nm}^{-2}$. The detailed derivations
5 are mentioned in Appendix. If the F^- and Y^{3+} ions have the same effective radius r_e and
6 construct one closely packed F+Y monolayer, r_e can be calculated to be 0.144 nm . This
7 radius is near the literature radius $r_{\text{F}} = 0.133 \text{ nm}$ and is not very far from the literature radius
8 of Y^{3+} (0.102 nm).⁶⁴⁾ Considering the Coulomb repulsion of negative F^- ions one another in
9 the monolayer, the calculated r_e value seems to be reasonable. Furthermore, since R_{F} can be
10 expressed as

$$11 \quad R_{\text{F}} = \frac{\sigma_{\text{F}}}{\rho\lambda' \sin \theta + \sigma_{\text{mY}}} \quad (1)$$

12 ρ is the atomic volume density of Zr + Y in YSZ and $\lambda' = \lambda - 2r_{\text{F}}$, where λ' is an effective
13 escape depth of λ subtracted by one F^- ion size in the case of one monolayer on the
14 DIW-rinsed YSZ layer. From eq. (1), we obtain an R_{F} of about 0.38, using the above
15 estimated values of σ_{F} and σ_{mY} . This R_{F} value is not far from the experimental saturation
16 value of ~ 0.5 . Their difference may be ascribed to the used assumptions. With respect to
17 bonding, for example, a hydrogen bond is formed to connect two F ions, the number of F
18 ions attracted by Y^{3+} ions (i.e., coordination number) would be more than 2 for σ_{YF} or/and 3
19 for σ_{mY} , and so on. Furthermore, there is a possibility that the used λ' value would be not well
20 approximated. Thus, it can be said that the model of one F+Y monolayer formation is
21 roughly valid. That is, F and Y ions in the monolayer would be so arranged that the layer
22 packing density is be maximized. When R_{YA} is nearly more than 0.2, the highest density may
23 be achieved and no more F and Y ions could get into the layer.

24 During sample preparation and transportation prior to Si film deposition, contaminants

1 from the laboratory atmosphere adsorb on the surface of the chemically cleaned YSZ layer.
2 At $R_{YA} \geq 0.15$, R_F is more than ~ 0.45 , such that the chemically adsorbed F covers the YSZ
3 surface almost fully, as mentioned above. Thus, the F+Y monolayer acts as a layer that
4 protects the clean YSZ surface from the contaminants. However, when R_{YA} is lower than
5 ~ 0.07 , R_F is less than 0.4 for not only the DIW-rinsed YSZ layer but also the ethanol-rinsed
6 YSZ layer. Under this condition, some local areas with an insufficient coverage of the F+Y
7 monolayer on the YSZ surface possibly allow the direct contact of contaminants from the
8 environment. Furthermore, the low quality of the YSZ surface with the low R_{YA} may induce a
9 higher level of adsorption of contaminants. Particularly, on the surface of the DIW-rinsed
10 YSZ layer, water H_2O and hydroxides $-OH$ may adsorb, as shown in Fig. 10(b).

11 When the substrate is heated up to the deposition temperature in the vacuum chamber
12 just before Si deposition, most of the residual adsorbed F atoms evaporate, while the excess
13 Y atoms remain, as mentioned in the previous report.³²⁾ At the same time, most of the
14 contaminants adsorbed on the F+Y monolayer may also evaporate; some of them chemically
15 react with F. When $R_{YA} \geq 0.15$, the clean surface of the YSZ layer appears with the
16 crystallographically ordered sites. Therefore, the crystallographic information regarding the
17 YSZ layer can result in the crystallization of the deposited Si film, which may be easier for
18 arriving Si atoms to nucleate even at low deposition temperatures, and we can obtain Si films
19 with high crystalline fractions on the YSZ layers with high R_{YA} values for both ethanol- and
20 DIW-rinse cases. On the other hand, for a low $R_{YA} < 0.07$, although the residual adsorbed F
21 atoms are evaporated by heating the sample, the surface of the YSZ layer is not as clean and
22 pure as the higher R_{YA} layer. Since R_F is smaller than 0.4, in particular, for the DIW-rinse
23 case, some areas of the YSZ surface directly react with the adsorbed contaminants; thus, they
24 may be modified into other phases and disordered. This reaction and modification may be
25 enhanced by the low crystalline quality of the YSZ surface with the low R_{YA} . The chemical

1 modification disturbs the transmission of the crystallographic information regarding the YSZ
2 surface to the arriving Si atoms. As a result, on the YSZ layers with the lower R_{YA} , Si
3 nucleation and the subsequent crystallization of Si films hardly occur. However, in the local
4 areas of the ethanol-rinsed YSZ layer, Si crystallization occurs, as shown in Figs. 1 and 2.
5 This is because F+Y monolayer islands are formed in the local areas of the YSZ surface; thus,
6 they can protect the bare surface from contaminants locally. The entire YSZ surface is
7 partially covered with the monolayer islands. The formation of the monolayer islands can be
8 observed in Fig. 6, where, for the ethanol-rinse case at around $R_{YA} = 0.06$, R_{YC} is obviously
9 larger than R_{YA} and R_F is around 0.3. At $0.1 \leq R_{YA} < 0.15$, since the coverage of one F+Y
10 monolayer on the DIW-rinsed YSZ layer is partial, X_C is also in transition from zero to the
11 saturated value.

12 As mentioned above, this mode can explain the experimental results qualitatively.
13 However, it is not sufficient and is not beyond speculation since we do not have any clear
14 evidence for the existence of contaminated areas at the interface under the amorphous Si
15 regions yet. Thus, we should further investigate the interface properties in more detail.

16

17 **5. Conclusions**

18 We investigated comprehensively the Y content and rinse solution dependences of the
19 crystallization of Si films deposited on glass substrates covered with poly-(111)YSZ layers at
20 deposition temperatures T_S lower than 550 °C. From the cross-sectional HR-TEM image of
21 the Si film deposited at 430 °C, it was found that some regions were crystallized directly on
22 the YSZ layer without an amorphous transition layer, where Si lattice fringes were tightly
23 connected to YSZ lattice fringes. Furthermore, it was found that the crystallization of the
24 deposited Si films occurred on YSZ layers at T_S lower than that on glass substrates without
25 YSZ layers by more than 100 °C. Therefore, it can be concluded that the poly-YSZ layer

1 induces and stimulates the crystallization of the deposited Si film at lower temperatures,
2 compared with the case of direct deposition on glass substrates. The impurity concentrations
3 of Y and F, which diffused from the YSZ layers into the Si films, were negligible and less
4 than 2×10^{16} and 1×10^{16} atoms/cm³, respectively. The Zr concentration in the film bulk was
5 $\sim 1 \times 10^{16}$ atoms/cm³, but that near the interface was relatively high, i.e., $\sim 5 \times 10^{18}$ atoms/cm³.

6 From the above-mentioned results, the crystallization mechanism was discussed. The
7 discussion leads to the next important suggestions on the method of obtaining a high
8 crystalline fraction of the Si film. 1) Prior to Si film deposition, the YSZ layer should be
9 chemically cleaned with a solution containing HF. By this treatment, the damaged and
10 disordered surface layer is removed, and then the surface is covered with adsorbed F atoms.
11 2) The Y content ratio of YSZ, R_{YA} , should be roughly more than 0.2. The amount of
12 adsorbed F atoms on the YSZ surface increases with R_{YA} and saturates at $R_{YA} \geq 0.15$. Thus,
13 $R_{YA} \geq 0.2$ may guarantee that one F+Y monolayer covers the clean YSZ layer fully, which is
14 sufficient for protecting the YSZ surface from contaminants in the atmosphere. Furthermore,
15 the crystalline quality and stability of the YSZ layer with $R_{YA} \geq 0.2$ are superior to those of
16 the layer with a low $R_{YA} < 0.07$. Therefore, it can be speculated that, at $R_{YA} \geq 0.2$, the
17 crystallographic information regarding the YSZ layers is smoothly transmitted to the
18 deposited Si films; thus, so that Si crystallization might be induced at lower temperatures.

19 From this study, it can be considered that the CI layer method is a useful direct
20 deposition technique for obtaining a crystallized Si film with a uniform crystalline quality
21 and no incubation layer at low temperatures in the entire deposition area. However, from now
22 on, we should work on reducing the Zr concentration for device performance and on
23 investigating the crystallographic relationship of each grain between the poly-YSZ layer and
24 the crystallized Si film on it.

25

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4

5 Appendix

6 Because YSZ is a CaF_2 crystal structure, ρ is $4/a^3$. Using ρ and the atomic volume density
7 of Y (ρ_Y), R_{YA} and R_{YC} can be expressed as

8
$$R_{YA} = \frac{\rho_Y}{\rho}, \quad (\text{A}\cdot 1)$$

9
$$R_{YC} = \frac{\rho_Y \lambda' \sin \theta + \sigma_{mY}}{\rho \lambda' \sin \theta + \sigma_{mY}}, \quad (\text{A}\cdot 2)$$

10 considering one F+Y monolayer on a DIW-rinsed YSZ layer. $\rho \lambda' \sin \theta$ is the area atomic Zr+Y
11 density of the YSZ layer under the monolayer in the measurement of XPS at $\theta = 35^\circ$.

12 Using eqs. (A·1) and (A·2), we obtain

13
$$\sigma_{mY} = \rho \lambda' \sin \theta \frac{(R_{YC} - R_{YA})}{(1 - R_{YC})}. \quad (\text{A}\cdot 3)$$

14 Next, we consider the number of Y^{3+} ions of the YSZ layer, which attract F^- ions in the
15 monolayer. It is assumed that the Y ions originate from the first and second Zr+Y atomic
16 layers of a cubic (100) YSZ on average. From this assumption, σ_{YY} is equal to $a\rho_Y = a\rho R_{YA}$;
17 thus, σ_F can be expressed as

18
$$\sigma_F = 3\sigma_{mY} + 2\sigma_{YY} = 3\sigma_{mY} + 2a\rho R_{YA}. \quad (\text{A}\cdot 4)$$

19 Per unit cell area of a^2 at $R_{YA} = 0.2$, we can estimate the average numbers of Y in one
20 monolayer and Y attracting F ions in the YSZ layer. That is, $a^2\sigma_{mY} \approx 0.52$ and $a^2\sigma_{YY} =$
21 $a^3\rho R_{YA} \approx 0.80$. Thus, the number of F ions per a^2 in one monolayer can be calculated as $a^2\sigma_F$
22 ≈ 3.2 .

23 On the other hand, if the F^- and Y^{3+} ions have the same effective radius r_e and
24 construct one close-packed F+Y monolayer, $\sigma_F + \sigma_{mY}$ can also be expressed with r_e as

1

$$\sigma_F + \sigma_{mY} = \frac{1}{2\sqrt{3}r_e^2}. \quad (\text{A}\cdot 5)$$

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21

1 Figure captions

2

3 Fig. 1. (Color online) Raman spectra of the Si films deposited on the (a) ethanol-rinsed and
4 (b) DIW-rinsed YSZ layers. For comparison, (a) and (b) show the spectra from the Si films
5 deposited on the ethanol-rinsed and DIW-rinsed glass substrates, respectively.

6

7 Fig. 2. (Color online) Y content R_{YA} dependences of the crystalline fractions X_C of the Si
8 films deposited at 430 °C on the ethanol-rinsed and DIW-rinsed YSZ layers. Squares and
9 triangles indicate the ethanol-rinse and DIW-rinse cases, respectively. Each plotted datum
10 shows the average of 3 to 5 measurement points of one sample. The top and bottom error
11 bars indicate the maximum and minimum values, respectively.

12

13 Fig. 3. (Color online) *In situ* RHEED patterns of the (a) bare YSZ layer at 430 °C and (b)
14 1-nm-thick, (c) 10-nm-thick, and (d) 60-nm-thick Si films deposited on the DIW-rinsed YSZ
15 layers with $R_{YA} = 0.13$ at $T_S = 430$ °C. The patterns were taken sequentially during the Si film
16 deposition. As a reference, (e) shows a pattern from an amorphous Si film.

17

18 Fig. 4. (Color online) Cross-sectional TEM images of the Si film deposited at $T_S = 430$ °C on
19 the DIW-rinsed YSZ layer with $R_{YA} = 0.21$, where (a) is a low resolution and (b) is a high
20 resolution (HR). The HR-TEM image (b) shows a close-up image of the dotted square frame
21 around the interface in (a). The electron-diffraction patterns simulated based on the local
22 lattice images enclosed by the white (point 1) and black (point 2) square frames are also
23 shown. As for the local areas labeled as points 1 to 4, please refer to the main text.

24

25 Fig. 5. (Color online) (a) XPS survey spectra from the (i) as-deposited, (ii) HF-dipped, and

1 (iii) DIW-rinsed YSZ layers. The R_{YA} of the YSZ layers is 0.13. The notable points indicate
2 the differences in the peak intensities of F and Y among the three spectra.

3

4 Fig. 6. (Color online) (a) Dependences of the Y content ratios of the chemically treated YSZ
5 layers, R_{YC} , on R_{YA} . (b) Dependences of the F ratios of $F/(Zr+Y) = R_F$ on R_{YA} . The chemical
6 treatment used were the HF dipping process, the ethanol rinsing process after the HF dipping
7 process, and the DIW rinsing process after the HF dipping process.

8

9 Fig. 7. (Color online) Concentration depth profiles of (a) Zr and Y, and (b) O and F in the
10 120-nm-thick Si film deposited on the ethanol-rinsed YSZ layer, and (c) O and F in the
11 60-nm-thick Si film deposited on the DIW-rinsed YSZ layer. They were measured by SIMS.
12 As a reference, the Si secondary ion intensity is shown in each figure. The deposition
13 temperature was 430 °C and the R_{YA} values for (a) and (b), and (c) were 0.08 and 0.16,
14 respectively.

15

16 Fig. 8. (Color online) Deposition temperature dependences of the Si crystalline fractions for
17 ethanol-rinse case. Closed and open squares indicate the results for the Si films deposited on
18 the ethanol-rinsed YSZ layers with $R_{YA} \gtrsim 0.13$ and on the ethanol-rinsed glass substrates,
19 respectively.

20

21 Fig. 9. (Color online) SEM images of the Secco-etched Si films deposited on the
22 ethanol-rinsed YSZ layers at $T_S =$ (a) 320, (b) 350, and (c) 430 °C, where the samples are the
23 same as those in Fig. 8. In (c), the hole indicated by an arrow was formed by Secco-etching a
24 local amorphous region.

25

1 Fig. 10. (Color online) (a) Narrow-scan XPS spectra of the Zr 3d from the DIW-rinsed YSZ
2 layers with the high $R_{YA} = 0.21$ and low $R_{YA} = 0.07$. The RHEED pattern in the upper right
3 was taken from the DIW-rinsed YSZ layer with $R_{YA} = 0.07$ at 430 °C just before the Si film
4 deposition. (b) Narrow-scan XPS spectra of the Y 3d from the DIW-rinsed YSZ layers with
5 the high $R_{YA} = 0.21$ and low $R_{YA} = 0.07$, and from the ethanol-rinsed YSZ layer with the low
6 $R_{YA} = 0.06$. For comparison, the Zr 3d and Y 3d spectra of the as-deposited YSZ layer with
7 $R_{YA} = 0.21$ are shown in (a) and (b), respectively.

8

9 Fig. 11. (Color online) Schematic model of crystallization mechanism of the Si films
10 deposited on the ethanol-rinsed YSZ layers with the high and low R_{YA} , and on the
11 DIW-rinsed YSZ layers with the high and low R_{YA} .

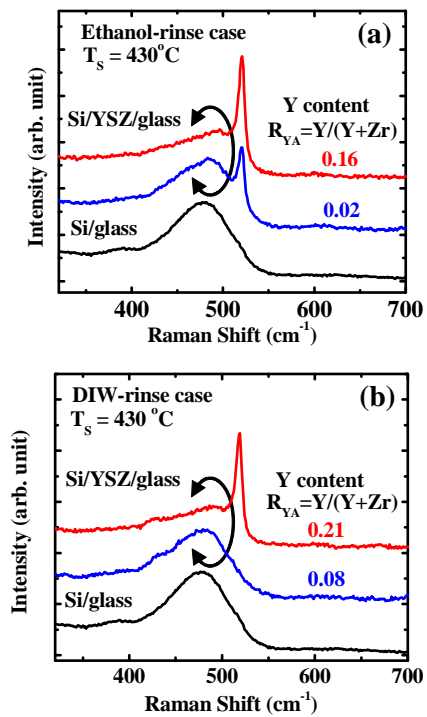


Fig. 1

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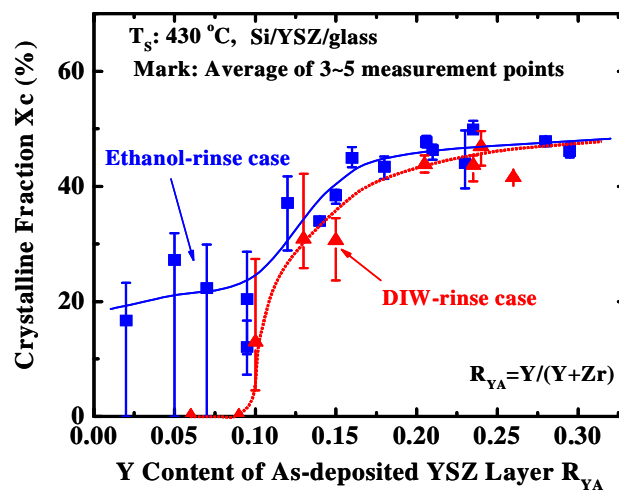


Fig. 2

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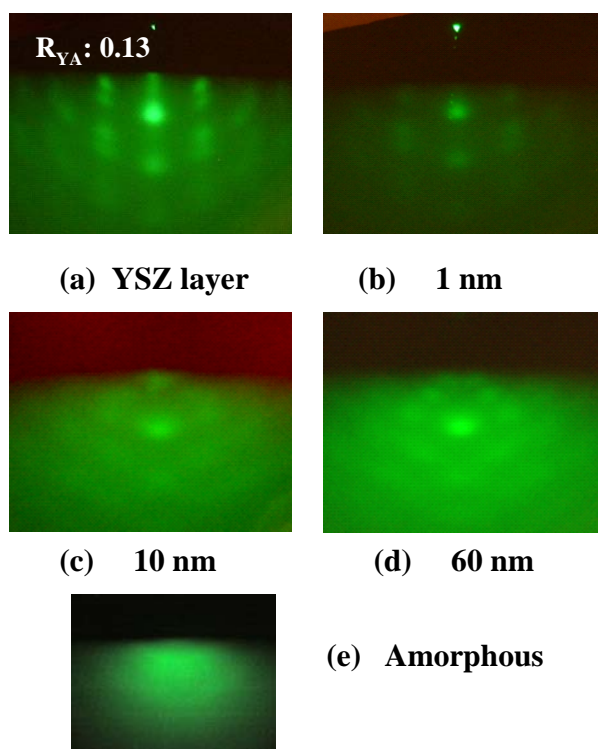
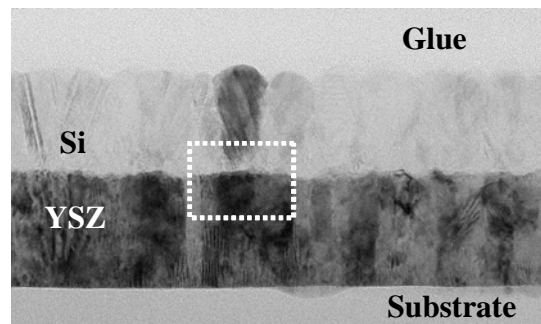
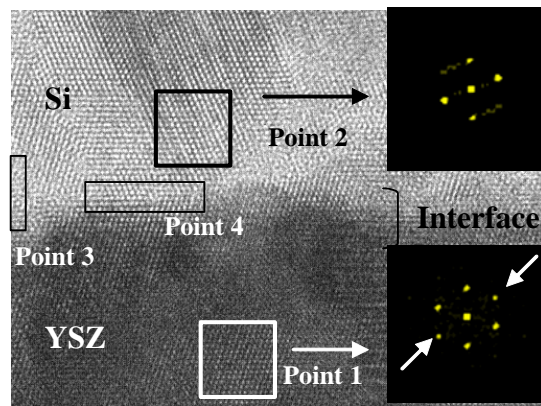


Fig. 3

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(a) 



(b) 

Fig. 4

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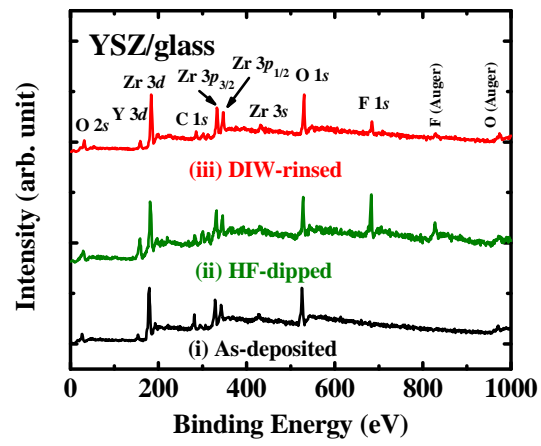


Fig. 5

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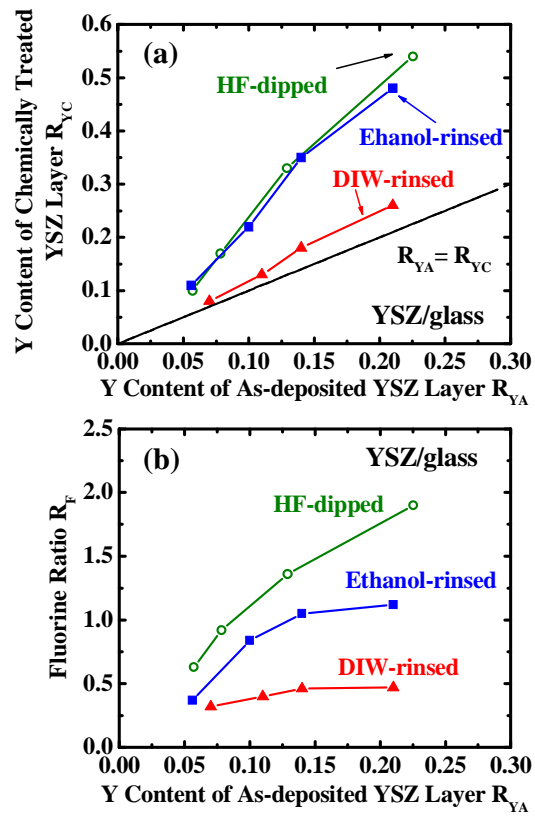


Fig. 6

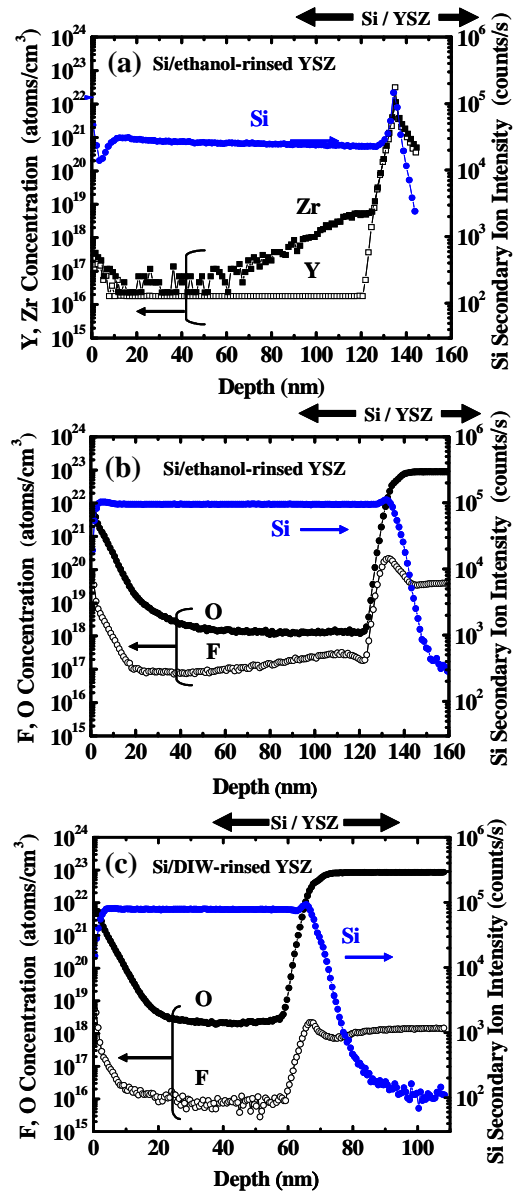


Fig. 7

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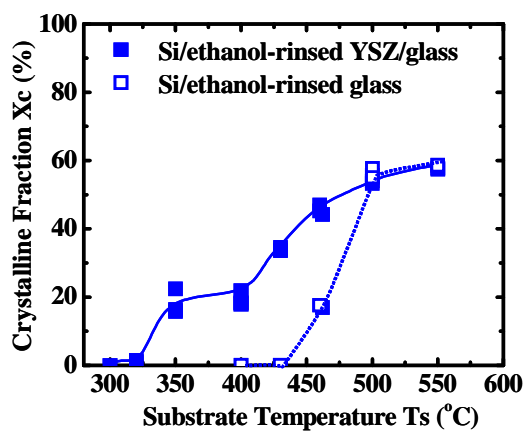


Fig. 8

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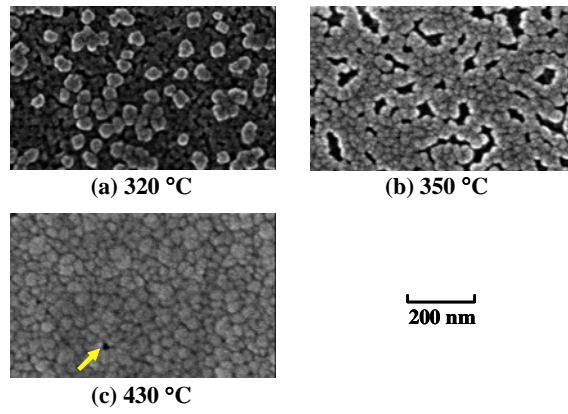


Fig. 9

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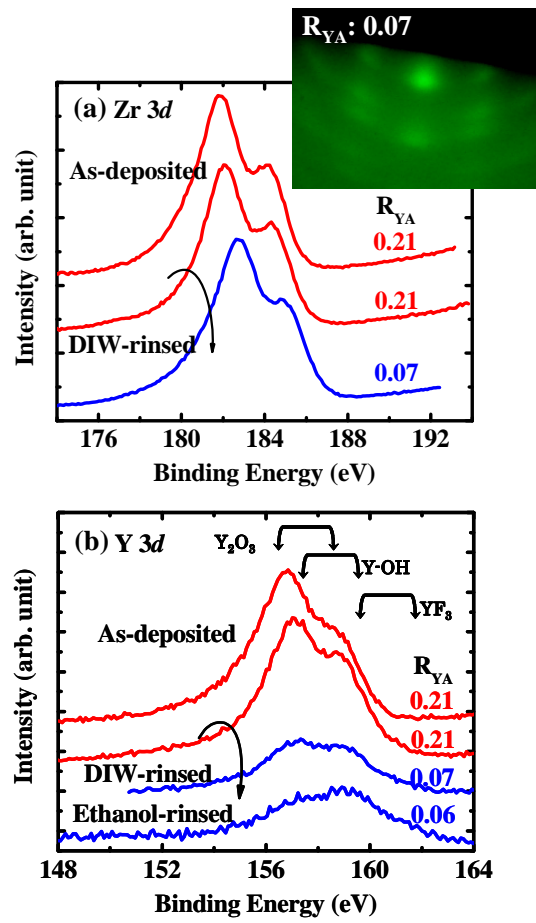


Fig. 10

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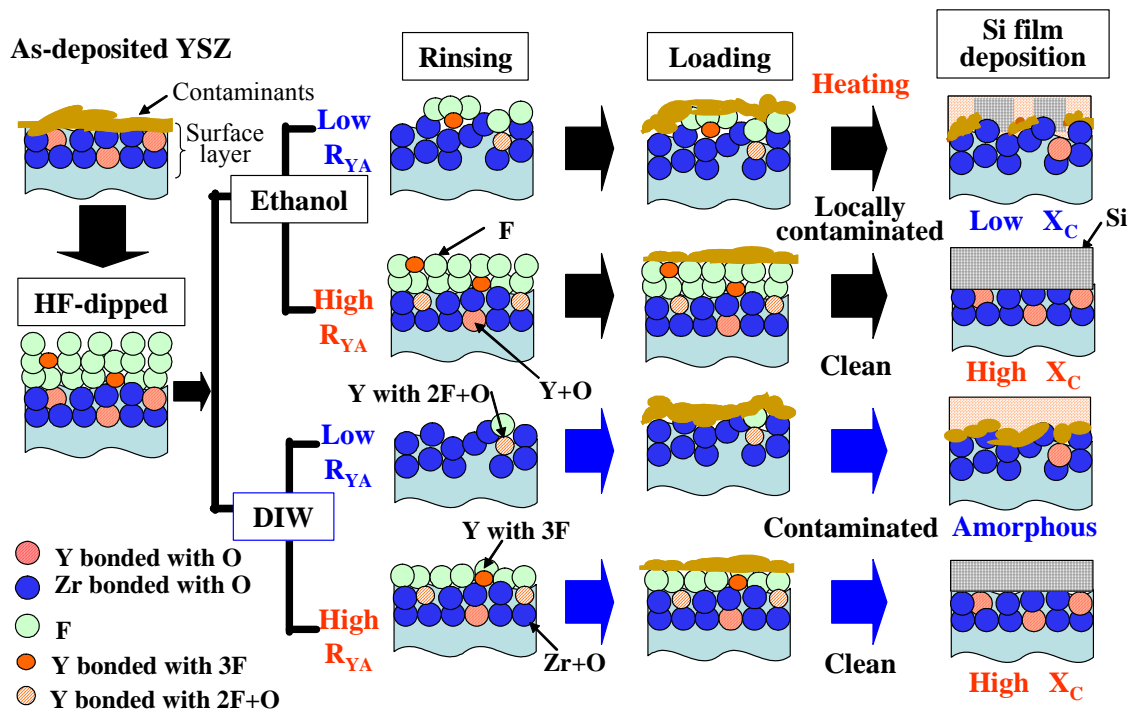


Fig. 11

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