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Description	

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Low Temperature Deposition and Crystallization of Silicon Film on an HF-etched Polycrystalline Yttria-Stabilized Zirconia Layer Rinsed with Ethanol Solution

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Abstract

As an induction layer for Si crystallization, an yttria-stabilized zirconia (YSZ) film was deposited on a glass substrate. The YSZ layer, already etched with HF and rinsed with ethanol, was heated to 430 ^{o}C. The Si film deposited on it was partially crystallized. This was confirmed by transmission electron microscope. The crystallization fraction was greater than that on a YSZ layer rinsed by deionized water. Without using YSZ layer, deposited Si film was amorphous. F atoms in HF-etching solution were adsorbed on the YSZ layer and remained even after the ethanol rinse. These remaining F may be important for crystallization.

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Polycrystalline Si (poly-Si) and microcrystalline Si films on non-heat resistant glass substrates are very useful not only for thin film transistors (TFTs) applied to active matrix flat panel displays, but also for photovoltaic devices such as solar cells. In order to obtain the poly-Si film by deposition directly on the substrate at a lower temperature than usual Si processes, it was proposed to use an induction layer for crystallization (crystallization-induction layer : CI layer),[1-3] to cover the surface of the substrate. This CI layer was expected to provide nucleation sites to induce or stimulate crystallization of deposited Si. This method seemed to have the potential to lower crystallization temperature of Si film, compared with the conventional method without using CI layer. This CI-layer method was expected to produce crystallized films of high quality with low impurity content and low surface roughness, for high mass production. As crystallization-induction materials, ZrO_2[1] and CaF_2[2,3] were proposed. However, the ZrO_2 layer induced an amorphous incubation layer, and CaF_2 was not a proper material for Si electron devices due to its low breakdown field and fluoride trap charges.

In our case, a polycrystalline yttria-stabilized zirconia ($(ZrO_2)_{1-x}(Y_2O_3)_x$: YSZ) film was used because YSZ is thermally and chemically stable, and has a cubic crystal structure with a relatively small lattice mismatch of about 5% with Si. Also, it has been reported that an Si film is heteroepitaxially grown on a YSZ substrate[4] and vice versa.[5] Although, at such a low deposition temperature, heteroepitaxial growth of Si is not expected, the same crystal structure and small lattice mismatch with Si are favorable factors for stimulation of Si film crystallization. Previously, we reported that a deposited Si film was crystallized at 515 ºC on a (111) YSZ layer deposited on a glass substrate, whereas Si film deposited without YSZ layer was amorphous.[6] Lately, we reduced the crystallization temperature to 430 ºC by using a YSZ layer cleaned with diluted HF and ethanol solutions before depositing Si film.[7,8]

In this paper, we show by high resolution transmission electron microscopy (HR-TEM) that

various regions of the 430 ^{o}C-deposited Si film were crystallized directly on the HF-etched and ethanol-rinsed YSZ layer without amorphous transition region. It is also shown that the ethanol rinse process is superior to the deionized water (DIW) rinse process. Based on X-ray photoelectron spectroscopy (XPS) analysis, which reveals the surface chemical states of the YSZ layers, we discuss the mechanism of the low-temperature crystallization of the Si film on the ethanol-rinsed YSZ layer.

The substrate was a 2×1 cm^2 quartz substrate covered with a 70-nm-thick polycrystalline (111) YSZ layer which was deposited by reactive magnetron sputtering with Ar + O_2 mixed gas. The sputtering target was a Zr metal target, on which 8 pieces of 1×1 cm^2 Y were placed in a circular arrangement. The atomic ratio of Y to Zr+Y, Y/(Zr+Y), was estimated to be 0.10 to 0.17 by XPS. The YSZ layers were chemically cleaned prior to deposition of Si film, as shown in Fig. 1. At first, each sample was pre-cleaned ultrasonically with ethanol solution and DIW for 3 min individually, in sequence. After that, in order to remove the contaminated and damaged surface layer of the as-deposited YSZ film, the sample was dipped in 5% HF solution for 3 min. The HF-etching process is necessary because, without it, a deposited Si film was amorphous at the deposition temperature T_s of 430 ºC in this study. Next, one of two kinds of rinse processes was performed. One process used DIW for 3 min (conventional process), and the other process used ethanol solution for 3 min. Immediately after the rinse process, a ~60-nm-thick Si film was deposited by electron beam evaporation method at T_s = 430 ºC, at a deposition rate of 1 nm/min in ~2×10^{-6} Pa. The degree of crystallization of the deposited Si film was evaluated by Raman spectroscopy, and the film growth of deposited Si from its interface of the YSZ layer was observed by HR-TEM. The surface chemical states of the YSZ layers were evaluated by XPS method at a 35^{o} take-off angle, using Al Kα (1486.6 eV) as an X-ray source.

Figure 2 shows the Raman spectra of the Si films deposited on the YSZ layers (Si/YSZ/glass)

rinsed with ethanol and DIW, compared with the Si film deposited on the glass substrate (Si/glass) rinsed with ethanol. On the right-hand side, for the ethanol-rinsed YSZ layer, the HR-TEM image shows a close-up of one area on the interface together with the electron-diffraction (ED) patterns. The ED patterns were simulated by using the fast Fourier transform (FFT) based on the local lattice images which are enclosed by the square white frames. A broad peak around ~480 cm^{-1}, which indicates amorphous Si phase, appears mainly in the Raman spectra of the Si films on the DIW-rinsed YSZ layer, and on the ethanol-rinsed glass substrate. The spectrum for the DIW-rinsed layer also shows a small peak at 517 cm^{-1}, which indicates crystal Si phase. However, the spectrum of the Si film deposited on the ethanol-rinsed YSZ layer shows a large sharp peak at 517 cm^{-1}, in addition to the broad peak of amorphous phase, which means that a larger fraction of the Si film was crystallized than in the case of DIW-rinsing. Also, from the TEM image, it can be seen that some large regions of the Si film were crystallized directly from the YSZ layer, without an amorphous transition region, although the other regions are in the amorphous phase, which corresponds to the Raman spectrum. The strong spots in both the ED patterns appear due to {111} planes, except for the two spots of YSZ {200} indicated by the white arrows. From these patterns, the crystallographic orientations normal to the interface are found to be the same as <111>, which is the preferential orientation of the YSZ layer. Also, the crystallization is considered to be stimulated and induced by the YSZ layer, although the crystallized Si region contains many defects, e.g., twins. From Fig. 2, we can say that the HF-etched YSZ layer is effective in inducing low-temperature crystallization of deposited Si on it, and that the ethanol is much better as a rinse solution than DIW.

Figure 3(a) shows the XPS survey spectra from the DIW-rinsed YSZ layer, ethanol-rinsed YSZ layer, and ethanol-rinsed YSZ layer heated to T_s = 430 ^oC in the vacuum chamber without deposition of Si film. It can be found from this figure that the peak intensity ratio of Y 3*d* to Zr

3*d* for the ethanol-rinsed YSZ layer is much larger than that for the DIW-rinsed layer, although both ratios before HF-etching are the same. Also, F peak from the ethanol-rinsed layer is much larger than that from the DIW-rinsed layer, whereas both the C peak intensities are similar. However, by heating the ethanol-rinsed YSZ layer, the peak intensity of F is much reduced, although the peak intensity ratio of Y to Zr is not changed very much, compared with this ratio in the ethanol-rinsed YSZ layer. This means that the adsorption F atoms are removed from the surface by heating the rinsed layer, although the Y atoms remain.

Figure 3 (b) shows the XPS spectra of Y 3*d* for the three kinds of samples, the as-deposited, DIW-rinsed, and ethanol-rinsed YSZ layers. The arrows in the figure indicate the literature values of binding energies (BE) of Y_2O_3[9,10] and YF_3.[9,11,12] From this figure, it is seen that although the spectra of the as-deposited and DIW-rinsed layers are composed mainly of Y_2O_3 phase, the spectrum of the ethanol-rinsed layer is composed of non-negligible and higher BE components in addition to Y_2O_3 phase. The main peaks of higher BE components correspond well to those of YF_3 as shown in this figure, and the other subcomponent may be a hydroxide.[10] Since the XPS spectra for both Zr and C did not show peak shift due to chemical bond with F, it is considered that F preferentially bonds with Y.

Table I shows the summary of chemical composition ratios of Y/(Zr+Y) and F/(Zr+Y) of the variously treated YSZ surfaces, where the values are estimated from the integrated intensities of Zr 3*d*, Y 3*d*, and F 1*s* peaks, using atomic sensitivity factors. The sample S1 was prepared for HF-etched surface. The sample S2 was for the DIW- and ethanol-rinsed surfaces after HF-etching, and the XPS spectra have already been shown in Fig. 3(a). The difference in Y/(Zr+Y) between as-deposited S1 and S2 is not crucial for physical phenomena in this surface analysis. The dependence of crystallization of the Si film on the chemical composition will be reported later. We did not observed any change in the Y/(Zr+Y) ratio due to pre-cleaning within

the measurement error of about ±10%. For S1, by the HF-etching process, the Y/(Zr+Y) ratio is increased by a factor of about 1.5. This is probably because HF solution preferentially etched Zr oxide to Y oxide, or that etched-out Y atoms were adsorbed again on the YSZ surface although both the oxides were etched. The F/(Zr+Y) ratio is, also, more than 1.5, and the F atoms were attracted by chemical adsorption from the HF solution during the etching process. For S2, due to the DIW-rinse process, the Y/(Zr+Y) decreases to 0.14 near the as-deposited value of 0.13 and the F/(Zr+Y) is greatly reduced to 0.43. In contrast to this, with the ethanol-rinse process, the Y/(Zr+Y) and F/(Zr+Y) are high, 0.28 and 1.74, respectively, as shown in Fig. 3(a). From this result, it can be said that the Y bonded with F are easily removed by DIW, but they are hardly removed by ethanol solution. This is probably because the dielectric constant of water [~78 at room temperature (RT)], which is three times larger than that of ethanol (~25 at RT), weakens the ionic bond strength between Y and F. However, by heating, the F/(Zr+Y) of the ethanol-rinsed YSZ layer is reduced to 0.32, which is lower than the ratio for the DIW-rinsed layer, although the Y/(Zr+Y) increases a little to 0.32.

According to the results shown in Fig. 3 and Table I, it is considered that the F atoms which were adsorbed on the rinsed YSZ surface played an important role in the low-temperature crystallization of the deposited Si film. F/(Zr+Y) >1 in Table 1 means that the total Zr and Y atoms of the YSZ layer may be effectively covered with F atoms after HF-etching, in the ethanol-rinse case. Various contaminants such as vapor, carbon oxide, etc. may be adsorbed on the F atoms covering the rinsed surface during the transportation of the sample to the Si deposition chamber. In other words, the many F atoms prevent the bare YSZ surface from being contaminated, which works as a protection layer. In the deposition chamber, the adsorbed F atoms are evaporated together with the contaminants by heating the substrate to T_s so that the clean YSZ layer appears. Therefore, arriving Si atoms can contact to the bare surface of the

poly-YSZ layer directly, which easily stimulates and induces crystallization of the Si directly from the YSZ layer. On the other hand, for the DIW-rinse case, the bare YSZ surface may be contaminated during transportation to the deposition chamber because of F/(Zr+Y) << 1 as shown in Table. I. The adsorption contaminants may have reacted with the YSZ surface layer during substrate heating, and a stable contaminated layer may have formed on it. This contaminated layer may impede direct crystallization of the Si film from the YSZ layer.

In conclusion, the ethanol-rinse process after HF-etching of the YSZ layer is effective for low temperature crystallization of Si film. We showed that the crystallized volume in the deposited Si film for the ethanol-rinsed YSZ was much larger than the volume for the DIW-rinsed YSZ, and that the direct crystallization without amorphous at 430 ^{o}C of Si film occurred in various regions due to the ethanol-rinsed YSZ. The essential point for this effect is speculated to be as follows: Many F atoms which are adsorbed on the YSZ layer due to HF-etching remain even after ethanol-rinsing, although a large fraction of them are removed by DIW-rinsing. These F atoms may protect the bare YSZ surface from exposure to contaminants in preparation atmosphere prior to depositing Si film.

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Figure captions

Fig. 1

Process flow for cleaning a YSZ layer which acts as a stimulator of Si crystallization. The XPS measurements were performed after the pre-cleaning, HF-etching, and rinsing processes. One of the ethanol-rinsed samples was measured by XPS, again, after being heated to T_s.

Fig. 2

Raman spectra of the Si films deposited directly on the HF-etched YSZ layers (Si/YSZ/glass) rinsed with DIW or ethanol solution, compared with the Si film deposited on the glass substrate (Si/glass) rinsed with ethanol. The right-hand picture is an HR-TEM image of the Si film deposited on the HF-etched YSZ layer rinsed with ethanol, and shows the diffraction patterns of the regions inside the white square frames. The dashed lines are eye-guides for distinguishing among the amorphous Si, crystallized Si, and YSZ regions. The diffraction patterns were simulated by the fast Fourier transformer (FFT) method.

Fig. 3

(a) XPS survey spectra from the DIW-rinsed YSZ layer, ethanol-rinsed YSZ layer, and ethanol-rinsed YSZ layer heated to T_s = 430 ^{o}C in the vacuum chamber without deposition of Si film. (b) XPS spectra of Y 3*d* for the three kinds of samples, as-deposited, DIW-rinsed, and ethanol-rinsed YSZ layers. The arrows indicate the literature values of the electron binding energies of Y_2O_3 and YF_3, where the left and right arrows for each compound are for $3d_{5/2}$ and $3d_{3/2}$, respectively.

Table I. Comparison of the chemical composition ratios of Y/(Zr+Y) and F/(Zr+Y) on the YSZ surfaces after the surface cleaning processes.

Sample	Ratio	As-deposited	HF-etched	DIW-rinsed	Ethanol-rinsed	Heated (Ethanol)
S1	Y/(Zr+Y)	0.17	0.27	-	-	-
	F/(Zr+Y)	0	1.89	-	-	-
S2	Y/(Zr+Y)	0.13	-	0.14	0.28	0.32
	F/(Zr+Y)	0	-	0.43	1.74	0.32

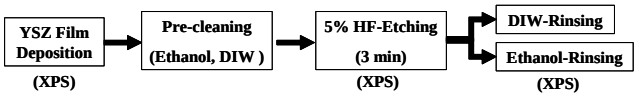
YSZ Film Deposition
(XPS)
Pre-cleaning
(Ethanol, DIW)
5% HF-Etching
(3 min)
(XPS)
DIW-Rinsing
Ethanol-Rinsing
(XPS)

Fig. 1

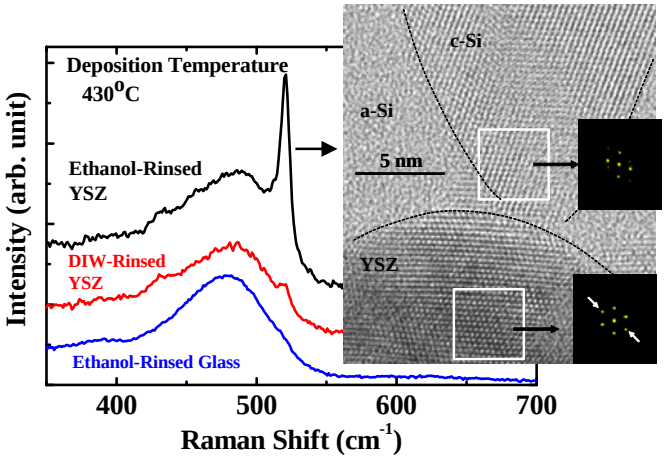
Deposition Temperature
430°C
Ethanol-Rinsed
YSZ
DIW-Rinsed
YSZ
Ethanol-Rinsed Glass
Intensity (arb. unit)
400
500
600
700
Raman Shift (cm-1)
c-Si
a-Si
5 nm
YSZ

Fig. 2

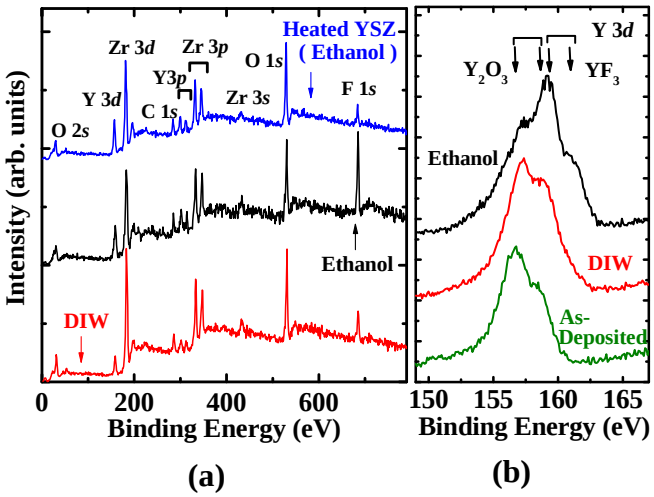
Intensity (arb. units)
Heated YSZ
(Ethanol)
Zr 3d
Zr 3p
O 1s
Y3p
Y 3d
C 1s
Zr 3s
F 1s
O 2s
Ethanol
DIW
0
200
400
600
Binding Energy (eV)
(a)
Y 3d
Y2O3
YF3
Ethanol
DIW
As-
Deposited
150
155
160
165
Binding Energy (eV)
(b)

Fig. 3