Direct Deposition of a Crystallized Si Thin Film on a YSZ/Glass Substrate at 430 °C

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Abstract— **A crystallized Si film was deposited at 430 °C by electron beam evaporation method on a glass substrate covered with a yttria-stabilized zirconia (YSZ) stimulation layer. The crystallization of the Si film was found to depend on the yttrium Y content of the YSZ stimulation layer, in which the crystalline fraction of the Si film increases with the Y content. Since the Y content influenced the crystalline quality of the YSZ layer, we speculate that the quality of the YSZ layer with the higher Y content is better than the lower one. Further, the adsorption of F atoms due to HF-dipping was higher on the YSZ layer with higher Y content. Thus, the clean high-quality YSZ surface is protected, which subsequently has an effect on the crystallization of the deposited Si film.**

Index Terms— **Silicon, crystallization, YSZ stimulation layer**

I. INTRODUCTION

Flat panel display technologies such as liquid crystal display and plasma display panel have been investigated for over 20 years as replacement for cathode ray tube. With the commercial success of active matrix liquid crystal display (AM-LCD), thin film transistors (TFTs) have received much attention in recent years for its function as pixel switches in AM-LCDs. Further into the future, where displays may be used not only in televisions and computer monitors, but also in billboards, electronic papers and so on, they must install transistors capable of data processing on the panel itself. Also, the fabrication process must not damage their non heat-resistant substrates such as glass or plastic. Though the hydrogenated amorphous silicon (a-Si:H) films have been used in the TFTs, their low electron mobility and poor stability make them not usable for logic devices. Thus, fabrication of crystallized silicon (c-Si) films are being researched extensively. The various methods have been proposed for low-temperature, e.g., metal induced crystallization (MIC) [1,2] and laser-annealing crystallization (LA) [3,4], they still have their own problems such as impurities due to remnant metals and non-uniformity of the electrical property in the films, which result in degradation of the TFT performance. To overcome these problems, we have proposed a method for low-temperature growth of a poly-Si film on a quartz substrate, where a poly-YSZ (yttria-stabilized zirconia : $(ZrO_2)_{1-x}(Y_2O_3)_x$) film is used as a stimulation layer to provide crystallographic ordered sites on the amorphous substrate and induce crystallization of the Si film during the deposition at a low-temperature [5]. YSZ is suitable for a stimulation material owing to the small lattice mismatch of only 5% as well as chemical and thermal stability. In fact, it has been reported that YSZ can grow heteroepitaxially on an Si substrate [6]. We have obtained a c-Si film at a deposition temperature as low as 430 °C by dipping the YSZ layer in HF solution and rinsing it with ethanol prior to the Si film deposition [7]. The crystalline fraction X_c of the deposited Si film increased with the increasing yttrium Y content of the YSZ layer [8]. By XPS measurement, we found that fluorine F atoms adsorbed on the YSZ layer due to HF-dipping, and that the amount of adsorbed F increased with the Y content of the YSZ layer. Therefore, we speculated that higher F adsorption provides better surface protection for a cleaned YSZ layer, and that, as a result, a higher crystalline fraction X_c of the deposited Si film was obtained. Since, by rinsing with deionized water (DIW), the adsorbed F atoms were removed much more than rinsing by ethanol, X_c of the Si film on the DIW-rinsed YSZ might be much inferior to that on ethanol-rinsed one [7]. Recently, however, on a DIW-rinsed YSZ layer with a high Y content, we obtained a similar high X_c with that on the ethanol-rinsed YSZ. This result indicates that crystallization of Si film is governed not only by amount of adsorbed F atoms. As we have reported that crystalline quality of the stimulation YSZ layer depends on the Y content [9], the YSZ quality may influence the Si crystallization. In this conference, we will discuss the effect of the crystalline quality of the DIW-rinsed YSZ layer on crystallization of the Si film at low temperature, including the effect of the adsorbed F atoms on the YSZ layer.

II. EXPERIMENTAL METHODOLOGY

A 70-nm-thick poly-YSZ layer was deposited by magnetron reactive sputtering on a quartz substrate at 50 °C. The yttrium Y content ratio (R_Y=Y(Y+Zr)) of the YSZ layer was varied from 0.05 to 0.21. The control method has been mentioned elsewhere [6]. Before the Si film deposition, the YSZ layer was treated by the series of chemical cleaning, as shown in Fig. 1. Every step in the chemical treatment was done in 3 min. A 60-nm-thick Si film was deposited by electron beam evaporation method at 430 °C. The crystalline

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quality of the YSZ film was measured by x-ray diffraction (XRD) method. R_Y was estimated from the intensities of Y 3*d* and Zr 3*d* peaks of the x-ray photoelectron spectroscopy (XPS) spectra which were normalized by the atomic sensitivity factor. The crystallinity of the YSZ layer surface prior to the Si film deposition was evaluated by reflection high-energy electron diffraction (RHEED). The crystalline fraction of the Si film was measured by Raman spectroscopy.

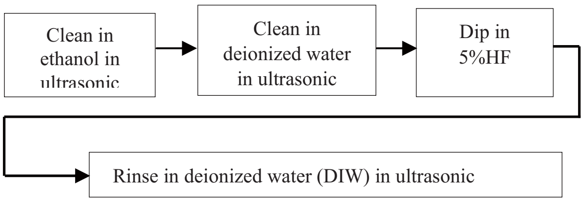

Figure 1. YSZ layer surface treatment process prior to Si film deposition.

III. RESULTS AND DISCUSSIONS

Figure 2 shows the Raman spectra of the Si films deposited at the substrate temperature of 430 °C on the DIW-rinsed YSZ stimulation layer with R_Y=0.21 and 0.08. In the spectrum of Si film on the YSZ with the low R_Y, only a broad peak around 480 cm^{-1} appears, which means that the Si film is not crystallized. However, in the spectrum of the Si film on the YSZ layer with higher R_Y=0.21, a sharp c-Si peak at 518 cm^{-1} appears, too, indicating that the Si film is crystallized. The R_Y dependence of the crystalline fraction of the Si film deposited on the YSZ layer is shown in Fig. 3. The fractions were calculated from the Raman spectra. The closed circles indicate average values of 3 to 5 measurement points and the error bars indicate the ranges between the maximum and minimum values. From this figure, it can be seen that the Si films on the YSZ layers with R_Y<0.1 are not crystallized, and that the crystalline fraction increases with R_Y and saturates when R_Y>0.2. The error bars are wider in the lower R_Y region, which means that the crystallization of the Si film is not uniform on the sample area at the lower R_Y, and vice versa. These results indicate that the crystallization of the Si film is highly dependent of the Y content of the YSZ stimulation layer.

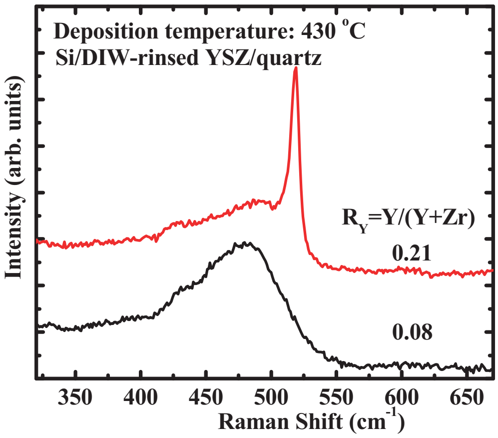

Figure 2. Raman spectra of Si films deposited at 430 °C on YSZ layers with different Y content (R_Y).

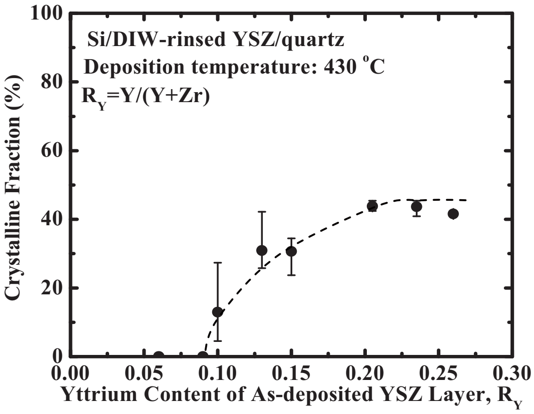

Figure 3. Y content dependence of Si film crystalline fraction. The closed circles indicate the average value of 3 to 5 measurement points and the error bars indicate the ranges between the maximum and minimum values.

Although we do not expect epitaxial growth of the Si film on the YSZ stimulation layer due to the low deposition temperature, we expect that the crystallographic information of the stimulation layer transmits to deposited Si film so that it may stimulate the crystallization of the Si film even at lower temperature. Thus, it can be considered that the crystalline quality of the YSZ layer may affect the crystallization of the deposited Si film. Figure 4 shows the XRD patterns of the YSZ stimulation layers as reported in [9]. It can be seen that the crystal structure of the YSZ layer varies with the Y content. At R_Y=0.02, the crystal structure is monoclinic. But, when R_Y are increased to 0.08 and 0.21, the YSZ layers transform to more stable phases of tetragonal and cubic, respectively. Also, the crystalline quality at R_Y=0.02 is much poorer than at the higher R_Y. Figures 5 (a) and (b) are

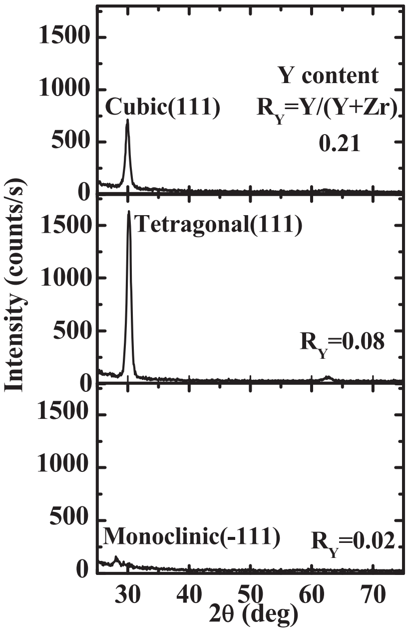

Figure 4. XRD patterns of the YSZ layers with various Y content as reported in [9].

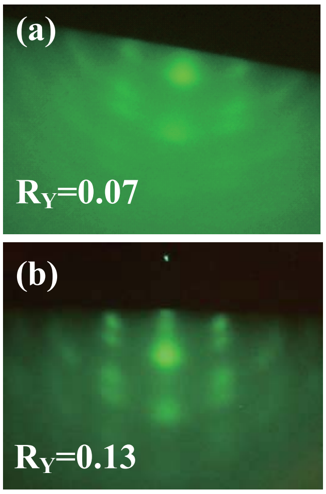

Figure 5. RHEED patterns of the YSZ layers with RY=0.07 (a) and 0.13 (b) at 430 °C, just before the deposition of the Si films.

the RHEED patterns from the surfaces of the YSZ layers with R_Y=0.07 and 0.13, respectively, which was monitored prior to the Si film deposition. We can see the spot patterns for the higher Y content are clearer than those for the lower content. This means that the crystalline quality of the surface of the YSZ layer with larger R_Y is better than the smaller one.

In order to investigate the effect of R_Y on the chemical state of the YSZ surface, we measured, by XPS, the DIW-rinsed YSZ layers with R_Y=0.21 and 0.07, whose spectra are shown in Fig. 6 (a) and (b), respectively. In these figures, we observe a peak of F 1*s*, which did not appear in the spectrum of the as-deposited YSZ surface. The F atoms adsorbed on the YSZ layer during the HF-dipping process and they were not totally removed even by the DIW-rinsing. The calculated F ratios to the total of Zr and Y, R_F=F/(Y+Zr), were 0.33 and 0.47, for R_Y=0.07 and 0.21, respectively. From these ratios, it can be seen that the larger amount of F atoms adsorb on the layer with the higher Y content. The narrow scan spectra of the Y 3*d* peaks form the samples of the spectra (i) and (ii) in the Fig. 6(a) are shown in the spectra (iii) and (iv) in the Fig. 6(b), respectively. The Y 3*d* peaks are mainly composed of Y_2O_3 phase, but with an addition of some small subcomponents, e.g., Y-OH around the higher binding energies. These components may disturb the order of the crystal structure and promote undesired chemical reaction with contaminants from the preparation atmosphere. It can be seen from Fig. 6(b) that the higher binding energy components for the low R_Y=0.07 are apparently larger than those for the high R_Y=0.21.

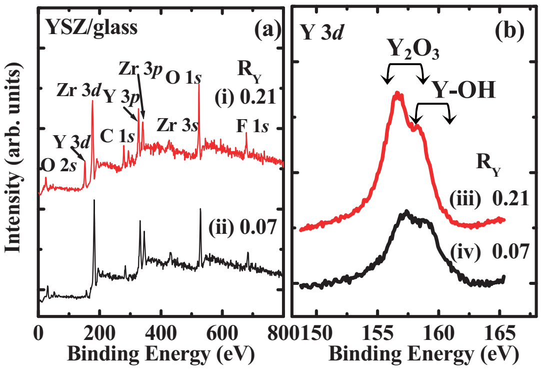

Figure 6. XPS survey spectra (a) from the DIW-rinsed YSZ layer surfaces with R_Y=0.21 (i) and 0.07 (ii). The narrow scan spectra (b) of Y 3*d* (iii) and (iv) from the surfaces of (i) and (ii), respectively. The arrows indicate the literature values of the binding energies of Y for Y_2O_3 and Y-OH compounds.

From these results, we discuss the crystallization model of the Si film on the DIW-rinsed YSZ layer. The HF-dipping removes the damaged and contaminated regions of the as-deposited YSZ surface and provides Si nucleation sites on it, and simultaneously many F atoms adsorb on the YSZ surface. Although by DIW-rinsing many of them are removed, the number of F atoms covering the YSZ layer with the higher R_Y is larger compared with the lower R_Y, so that it may be better for protection of the clean YSZ surface. Furthermore, the surface quality of the YSZ layer with the lower R_Y is poorer and chemically more active than the higher one. The poor quality surface induces contaminant adsorption from the atmosphere and oxidation of the arriving Si atoms during the deposition, resulting in the disturbance of the nucleation of the Si and subsequently its crystallization. Thus, the low-temperature crystallization of the Si film on the DIW-rinsed YSZ layer with the higher R_Y is easier to occur compared with that on the lower one.

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