[Technical Paper]

Homogenizing and Applying Dielectric Film to Wafer-Level Film Preparation

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(Received June 28, 2012; accepted November 8, 2012)

Abstract

MEMS devices such as piezoelectric devices are being used for various purposes in recent years. At the same time, silicon wafer diameters have been expanding for the purposes of mass production and cost reduction in the manufacture of these devices. Therefore, it is becoming more difficult to prepare a dielectric film with homogeneous thickness and electrical properties on the wafer. Generally, physical vapor deposition (PVD) methods such as sputtering are said to be comparatively reproducible for preparing films on large wafers, but these methods require expensive equipment. Metal organic decomposition (MOD), a chemical solution deposition (CSD) method, was used to form a PZT ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) film on the 4-inch wafers in this study because it does not need expensive equipment such as a vacuum system. To improve the ferroelectric properties of the film formed using the MOD method, we optimized the process parameters using design of experiments methods and found that temperature is the most significant control factor. A PZT film was prepared homogeneously on 4-inch wafers under optimum conditions. Furthermore, a more homogeneous PZT film was prepared by making the temperature uniform using a soaking cover. We think that these results can be applied to the preparation of films on larger wafers as an alternative to PVD methods, which are currently the main method of preparing dielectric films but which require expensive equipment.

Keywords: PZT, MOD, MEMS, Homogeneity, Ferroelectric

1. Introduction

MEMS devices such as piezoelectric devices are being used for various purposes in recent years. In MEMS device manufacturing, the diameter of the silicon wafer used has been expanding in order to facilitate mass production and cost reduction. Thin films, such as metal or ferroelectric films, are produced on these large wafers and devices are then formed using micromachining processes like photolithography. However, it is very difficult to prepare dielectric films with the requisite homogeneous thickness and electrical properties on large wafers because of problems such as residual stress,[1] and therefore, the reliability of the devices deteriorates in the course of these processes. Generally, physical vapor deposition (PVD), such as sputtering, and metal organic chemical vapor deposition (MOCVD) are said to be comparatively reproducible when preparing dielectric film on large wafers, but

these methods require very expensive and large-scale equipment such as vacuum systems. Therefore, metal organic decomposition (MOD), a chemical solution deposition (CSD) method, was used for the preparation of the dielectric thin film in this study. Besides not requiring expensive equipment, this method also has other advantages in that large-area films can be obtained and the composition can be easily controlled. The MOD method, however, has problems of low homogeneity of the electrical properties and the difficulty of controlling many process parameters. Therefore, the objective of this study was to solve these problems and apply this method to 4-inch wafer film formation. We evaluate the significance of the parameters and homogeneity of the film quantitatively for this objective. In our experiments, we used lead zirconate titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$, PZT) as the dielectric film because it is one of the most common materials used for MEMS

applications.[2]

2. Experiments

2.1 Optimization of process parameters

The MOD process parameters were optimized by design of experiments to improve the electrical properties and the crystal orientation of the film. We also identified significant parameters by analysis of variance. Design of experiments and analysis of variance are statistical and mathematical methods for conducting efficient experiments and are used in various studies such as the optimization of sputtering or CVD conditions.[3–6] Using these methods, we can not only optimize parameters but also determine which parameter has the largest effect on properties.

First, a SiO_2 film about 300 nm thick was formed on a 4-inch silicon wafer as an insulating layer using an oxidation furnace. Then, Ti and Pt were sputtered as an adhesion layer and a bottom electrode. The thicknesses of the Ti and Pt were approximately 5 nm and 150 nm, respectively. After sputtering, the 4-inch Pt/Ti/ SiO_2 /Si substrate was diced to 20 mm $\times$ 20 mm chips and these were ultrasonically cleaned in pure water, 2-propanol, and acetone. A PZT film was then prepared on these substrates using the MOD method, which consists of two processes: spin-coating, and rapid thermal annealing (RTA). First, the PZT solution (Kojundo Chemical Co.), which consists of PbO , ZrO_2 , TiO_2 and organic solvent, was spin-coated at 2,500 rpm for 20 s. The molar ratio of $\text{PbO}:\text{ZrO}_2:\text{TiO}_2$ is 120:52:48 and the mass concentration of these oxides is 10% or 20% in total. The sample was then annealed in air at 120°C for 2 min (evaporation of organic solvent), 250°C for 5 min (precursor formation) and 600°C or 700°C for 2 min (crystallization of the PZT). As shown in Table 1, three parameters (the crystallization temperature in RTA, the heating rate in RTA, and the mass concentration of the PZT solution) were varied in these processes to optimize these parame-

ters. The spin-coating and RTA processes were repeated ten times to prevent leaks in each experiment. The thickness of the film using 10 wt% solution was 1.3 μm and that using 20 wt% solution was 2.5 μm after 10 times coating.

After the PZT film was formed, each sample was etched by a buffered hydrofluoric etchant to expose the bottom electrode and Pt was sputtered for the top electrode. The properties of each sample were then measured. The full width at half maximum (FWHM) of the (100) peak of the X-ray diffraction (XRD) pattern of the films was measured to evaluate the crystal orientation. The dielectric constants and P-E hysteresis loops of the films were also measured. After that, the optimum conditions and significance of each parameter were investigated using analysis of variance.

2.2 Wafer level film preparation

Next, a PZT film was prepared on the 4-inch wafer under optimum conditions, and the thickness and electrical properties were investigated to evaluate the homogeneity of the film. The spin-coating and RTA processes were repeated ten times. To measure the thickness and electrical properties at various points on the film, holes were made in the PZT film using photolithography and Pt was sputtered using a metal mask. As shown in Fig. 1, the holes are located at 10 mm intervals. The top electrodes are also located at 10 mm intervals.

2.3 Measurement of temperature distribution

After this film preparation, the temperature distribution was measured in the RTA process because temperature was found to have a great effect on the film properties as will be explained later (3.1). The temperature was measured using a sample with seven thermocouples as shown in Fig. 2.

Various soaking covers, as shown in Fig. 3, were fabricated to keep the temperature uniform and homogenize the electrical properties of the PZT film. Three kinds of covers: carbon, quartz and stainless steel, were fabricated

Table 1 Parameters and levels for the optimization using design of experiments.

No.	Crystallization temperature in RTA (°C)	Heating rate in RTA (°C/min)	Mass concentration of the PZT solution (%)
1	700	400	20
2	700	100	10
3	600	400	10
4	600	100	20

Fig. 1 Pattern of the top electrode and the bottom electrode for the measurement of thickness and the electrical properties at various points on the film.

Fig. 2 Schematic diagram of the temperature measurement and the measurement points.

Fig. 3 Schematic diagram of the soaking cover.

to investigate the differences between materials, and the temperature distribution was measured inside each cover. Additionally, a PZT film was prepared on a 4-inch wafer using a quartz cover and its thickness and electrical properties were measured.

3. Results and Discussion

3.1 Results of optimization of process parameters

Figure 4 shows the result of the XRD analysis of each experiment described in Table 1. Table 2 shows the measurement results of each property. We optimized the process parameters and determined the significance of each parameter using analysis of variance.[7] We first analyzed each measured value in Table 2 according to the following equation,

$$y_{ijk} = m + a_i + b_j + c_k + e_{ijk} \quad (1)$$

where y_{ijk} is the combination of each parameter's level (i, j, k), m is the overall mean, a_i is the difference between m and the mean of the date in which the level of the parameter

Fig. 4 Results of the XRD analysis of each sample prepared under the condition described in Table 1.

A is i (b_j and c_k are similar), and e_{ijk} is the error. We next calculated the sum of squares of each parameter by summing up a_i^2 (or b_j^2 , c_k^2) of all dates and determined the unbiased estimate of variance by dividing the sum of squares by the degree of freedom (the number of levels - 1). The

Table 2 Results of the measurements of FWHM and the electrical properties of the film prepared under the condition described in Table 1.

No.	FWHM of (100) peak (deg)	Dielectric constant	Remanent polarization ($\mu\text{C}/\text{cm}^2$)	Coercive electric field (kV/cm)
1	0.23	1,520	10	38
2	0.26	1,685	14	46
3	0.31	1,407	30	61
4	0.24	1,277	31	60

Table 3 Optimum conditions of each parameter for FWHM and the electrical properties.

Factor	FWHM of (100) peak	Dielectric constant	Remanent polarization	Coercive electric field
Crystallization temperature in RTA ($^{\circ}\text{C}$)	700	700	600	700
Heating rate in RTA ($^{\circ}\text{C}/\text{min}$)	400	100	100	400
Mass concentration of the PZT solution (%)	10	10	10	20

Table 4 F values of each parameter for FWHM and the electrical properties.

Factor	FWHM of (100) peak	Dielectric constant	Remanent polarization	Coercive electric field
Crystallization temperature in RTA	2.25	221	80	21
Heating rate in RTA	6.25	Pooled	Pooled	Pooled
Mass concentration of the PZT solution	Pooled	71	Pooled	Pooled

Pooled means that the variation of the property by the change of the level of the process parameter is so small that the variation of the property is considered to result from not the change of the level of the process parameter but the error.

ratio of the unbiased estimate of variance of each parameter to that of the error is called the F value.[3] This value represents the effect of the parameter on the property and if it is larger than the reference value that has been calculated statistically, the parameter is a significant factor. Table 3 shows the optimum conditions for each property; FWHM, dielectric constant, remanent polarization, and coercive electric field. Table 4 shows the calculated F values.

For the dielectric constant, the F value of the temperature is larger than $F_1^1(0.05) = 161.4$, the reference of the F value at the 5% level with degrees of freedom of (1, 1). The F value of the temperature is larger than $F_2^1(0.05) = 18.51$ also in remanent polarization and coercive electric field, E_c . Therefore, the effects of temperature on these properties are statistically significant.

3.2 Results on wafer level film preparation

The PZT film was prepared on 4-inch wafers at 700°C because the optimum crystallization temperature was found to be 700°C for many properties as shown in Table 3. On the other hand, the heating rate and the mass con-

centration were found to have little effect on the properties and they were set at $400^{\circ}\text{C}/\text{min}$ and 20%, respectively, in order to promote fast formation of a thick film.

The thickness of the PZT was $1.6\ \mu\text{m}$ in approximately 64% of the overall area located around the center, and $1.5\ \mu\text{m}$ in the rest of the area nearer the rim. The dielectric constant, remanent polarization, and coercive electric field were globally $1,240 \pm 90$, $16.5 \pm 1.6\ \mu\text{C}/\text{cm}^2$, $34.6 \pm 2.7\ \text{kV}/\text{cm}$, respectively, as shown in Fig. 5 and Table 5. On the other hand, they were $1,290 \pm 70$, $16.5 \pm 1.2\ \mu\text{C}/\text{cm}^2$, $35.4 \pm 0.7\ \text{kV}/\text{cm}$ in the approximately 64% of the area around the center. We can conclude that PZT can be prepared homo-

Fig. 5 Measurement points for electrical properties of the wafer level film.

Table 5 Thickness and electrical properties of the wafer level film.

Point	Thickness (μm)	Dielectric constant	Remanent polarization ($\mu\text{C}/\text{cm}^2$)	Coercive field (kV/cm)
1	1.5	1,154	14.9	33.5
2	1.6	1,318	16.8	35.7
3	1.6	1,310	16.4	34.9
4	1.6	1,218	15.6	35.1
5	1.5	978	11.1	34.4
6	1.5	1,207	17.7	38.2
7	1.6	1,322	17.7	36.1
8	1.6	1,288	16.1	35.1
9	1.5	1,168	13.6	31.9
Global	1.5~1.6	1,240 $\pm$ 90	16.5 $\pm$ 1.6	34.6 $\pm$ 2.7
Central	1.6	1,290 $\pm$ 70	16.5 $\pm$ 1.2	35.4 $\pm$ 0.7

geneously around the center from these results. We also think that the temperature distribution in the RTA process affects the homogeneity of the dielectric property of the film, as shown in the next section. This is because the temperature was found to have a great effect on the properties, as shown from the results of the analysis of variance, and a more homogeneous film can be prepared if the temperature is made uniform.

3.3 Results on temperature distribution

The results of the measurement of temperature distribution in the RTA process are shown in Fig. 6. The temperature is widely distributed immediately after rapid heating with a maximum temperature difference of about 90°C. Even after several minutes, the temperature difference is about 25°C. Such temperature distribution is thought to

degrade the homogeneity of the electrical properties of the film; thus we devised a method of making the temperature uniform using a soaking cover as described in 2.3.

The results of the measurement of temperature distribution using a quartz cover are shown in Fig. 7 because the preliminary experiments showed that the temperature difference was the smallest when the quartz cover was used. The temperature distribution is small even immediately after rapid heating except at points 2 and 5, and the temperature difference is about 19°C within several minutes. This is smaller than the 25°C result of the measurement without a soaking cover. From these results, we concluded that a quartz cover could produce a more uniform temperature. Therefore, we next prepared and investigated a PZT film using a quartz soaking cover.

Fig. 6 Results of the measurement of temperature distribution in the RTA process.

Fig. 7 Results of the measurement of temperature distribution in the RTA process when a quartz cover was used.

Table 6 Thickness and electrical properties of the wafer level film prepared using a quartz cover.

Point	Thickness (μm)	Dielectric constant	Remanent polarization ($\mu\text{C}/\text{cm}^2$)	Coercive field (kV/cm)
1	2.3	1,083	7.3	30.2
2	2.4	1,285	14.5	30.8
3	2.4	1,295	14.9	28.6
4	2.4	1,266	15.4	29.2
5	2.3	1,076	14.9	33.1
6	2.3	1,278	12.2	26.3
7	2.4	1,360	15.0	29.6
8	2.4	1,338	13.8	27.0
9	2.3	1,354	15.8	28.9
Without cover	1.6	$1,240 \pm 90$	16.5 ± 1.6	34.6 ± 2.7
With cover	2.4	$1,310 \pm 50$	14.8 ± 1.0	29.0 ± 2.0

The thickness of the PZT film prepared using the quartz cover was $2.4 \mu\text{m}$ around the center and $2.3 \mu\text{m}$ near the rim. This was thicker than the film prepared without a cover in spite of using the same spin-coating condition and the same concentration of solution. We think this is because evaporation of the PZT solution was restrained by using an airtight cover. The dielectric constant, remanent polarization, and coercive electric field were $1,310 \pm 50$, $14.8 \pm 1.0 \mu\text{C}/\text{cm}^2$, $29.0 \pm 2.0 \text{ kV}/\text{cm}$, respectively, as shown in Table 6. Compared to the results shown in Table 5, we concluded that a PZT film can be homogenized by making the temperature uniform using a quartz cover.

4. Conclusions

In this study, the process parameters of the MOD method were optimized and, using analysis of variance, temperature was found to be the most significant factor quantitatively. Thus, a PZT film was prepared on 4-inch wafers under optimum conditions and measurement of its properties revealed that the PZT was homogeneously formed around the center. Furthermore, the temperature distribution in the RTA process was investigated in an effort to homogenize the film further. As our investigation revealed that temperature was widely distributed in the RTA process, we devised a method of making the temperature uniform using a soaking cover, and found that it made the film more homogeneous.

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