1. Introduction

Three-dimensional packaging using an embedded substrate is being developed to achieve miniaturization of the area for the capacitors in the electrical substrate. This embedded capacitor is manufactured for a three-dimensional structure rather than surface packaging technology. Embedded substrate technology is already used to some extent in the packaging process, but it mostly involves tip products rather than elements. Thin film capacitors, packaged into the electrical substrate, will become a new and useful technology in the near future. Generally, the preparation of a high-dielectric-constant film requires the use of heat treatment over 600°C. However, this high-temperature process causes serious damage to the electrical substrate that is popular for electrical products. Nano-transfer, therefore, could be a promising method for creating thin film capacitors because it involves preparation on a heat-resistive substrate followed by a transfer process onto the polymer substrate. [1] The concept of the method is shown in Fig. 1. This method consists of release and transfer processes. First, a capacitor is fabricated on an outer substrate that has high heat resistance, and it is then peeled from that substrate and transferred to the application substrate.

The principle examination procedures for the nano-transfer method have been confirmed for use with a Pt electrode, but a suitable quantitative structure design has not yet been found.

Among the various kinds of capacitor materials in use, lead zirconate titanate (PZT) systems are familiar, but materials containing lead will be replaced by other material systems. Barium titanate (BaTiO3) is one lead-free ferroelectric material and is used in this study.

In our previous studies, we fabricated PZT (Pb(Zrx,Ti1–x)O3) thin film capacitors to establish the process for the
nano-transfer method. However, there were some problems, such as thin films being destroyed during the film deposition process and not peeling off under some conditions. It is therefore necessary to clarify the main process parameters in the film preparation procedure for PZT.

On the other hand, BaTiO$_3$ film has higher internal stress than that of PZT because of the lower density of the raw solution materials. As a result, it is necessary to prepare another type of releasable substrate for the BaTiO$_3$ films. The weak adhesion force between the Pt and SiO$_2$ layer poses a difficulty for the transfer of prepared capacitors onto the polymer substrate. This is a common problem for ferroelectric films prepared on a releasable substrate using the metal organic decomposition (MOD) method. The internal stress of the films during the heating process causes the destruction of the structure. In a previous study, a Ti layer was introduced as the bonding layer between the Pt and SiO$_2$ in the prepared structure. However, the bonding of the Ti layer is too high to release the thin film capacitors in the release process. Therefore, it is necessary to optimize the thickness and design of the Ti layer to improve the film's characteristics and the nano-transfer method.

The purposes of this study are as follows: 1) Study the effect of heating on the deflection of the substrate and estimate the electrical properties of prepared films. 2) Confirm the effect of the double layer structure of the electrode and optimization of the shape of the electrode. 3) Clarify the relationships between PZT films and Pt in the releasing process.

2. Experimental Procedure for PZT (EXP-1)

2.1 Thin film fabrication process

Figure 2 shows the process of forming the PZT capacitor. A 4-inch Si wafer was used as the substrate. A 300 nm thick SiO$_2$ film was formed in an oxidation furnace. After that, the Si wafer was diced into 20 mm squares. Then, the Pt layer for the bottom electrode was deposited by sputtering. Pt was sputtered variously from thicknesses of 40 nm to 2,500 nm to investigate the relationship between the Pt thickness and the release property of the interface. PZT thin films were fabricated on the bottom electrode using metal organic decomposition (MOD). The MOD method is a chemical solution deposition (CSD) method that is similar to the sol-gel method. Unlike other thin film deposition methods, MOD does not need a vacuum, thus a thin film can be produced easily and at low cost. The PZT was deposited using a spin coater at 2,500 rpm and followed by rapid thermal annealing (RTA). The maximum temperature was 700°C. These MOD processes consisting of deposition and annealing were repeated 10 times to build up a thickness of 2,000 nm to 2,500 nm which would provide an adequate PZT thickness to prevent leakage current.

After the PZT thin films were formed, the Pt layer for the upper electrode was deposited. Figure 3 shows a schematic of the PZT capacitor.

2.2 Evaluation method

The structural, electrical and releasing properties of this capacitor were then measured. The structural properties were measured using x-ray diffraction (XRD). The electrical properties were measured with an LCR (inductance, capacitance and resistance) meter. The releasing properties were investigated using a tape peel test, a qualitative test method in which a tape affixed to the sample surface is peeled off. The Pt film stress was also measured to clarify its effect on the release property.

3. Experimental Procedure for BaTiO$_3$ (EXP-2)

3.1 Double-layered electrode structure

In a previous study, a double-layered electrode structure, consisting of two kinds of areas with and without the Ti layer, was prepared.[2] In this study, the Ti layer of the electrode structure is used to protect the release during
the heat treatment. The central area, without the Ti, is used for the releasable capacitor. The structure of the substrate is shown in Fig. 4 and is almost the same as that in Fig. 2.

However, only one kind of electrode design has been prepared up to now. It is shown in Fig. 5. It will be necessary to clarify a suitable structural design for the nano-transfer method that enables wider application. The target will be the development of another electrode structure that has more area for the Pt layer and high protection against destruction during the heating process. The establishment of a method to prepare BaTiO₃ capacitors at the chip scale will be another problem. Dicing after preparation at wafer scale was not successful because of the destruction of the structure. Development of a dicing process from wafer to chip is expected to be useful for improving production.

### 3.2 Preparation of the double-layered electrode structure for BaTiO₃ (EXP-2-1)

Several variations of capacitor chips composed of a double-layered electrode structure were prepared and heat treatment was applied to clarify their suitability in an expected process flow. Figure 6 shows the design of the prepared samples. Three designs were prepared: circular, square with rounded corners, and square. Three sizes were prepared: 12 mm, 14 mm and 16 mm.

Capacitor chips with a uniform lower electrode were also prepared using the same process for comparison with the above samples. Three kinds of Pt lower electrodes were prepared: 1) formed at room temperature, 2) formed at 200°C, and 3) formed as Pt on Ti at room temperature.

Figure 7 shows the process flow for preparing the lower electrode with the double-layered structure. This preparation was performed on wafer and diced into chips 20 mm × 20 mm. The capacitor film was prepared onto the above chip substrate.

BaTiO₃ films of 15 layers were prepared using MOD. The condition of the spin coater was 2,500 rpm for 20 seconds and the crystallization condition was 700°C for 3 minutes. The structure and electrical properties of the samples formed without destruction of the structure were evaluated. X-ray diffraction (XRD) analysis was conducted and the dielectric constant and film thickness were investigated.

### 3.3 Evaluation of the release depending of the design of the lower electrode (EXP-2-2)

Based on an assumption from the results of Exp-2-1, an additional experiment was performed to confirm that using Ti in the corner area protected the structure from destruction. We prepared four kinds of samples to clarify this. The designs are shown in Fig. 8. These are the designs of the lower electrode of the Pt and Ti layer. After the four kinds of electrodes were formed, BaTiO₃ films
were prepared onto the lower electrode, as shown in Fig. 7. The preparation process of the films was the same as used for Exp-2-1.

4. Experimental Results and Considerations

4.1 PZT (EXP-1)

4.1.1 Fabrication stability of capacitor

To investigate the stability of the thin film fabrication, the deposition temperature and film thickness conditions of the bottom Pt electrode layer were changed and PZT thin films were prepared on it.

On the sample with a Pt thickness of 1 µm and a deposition temperature of 200°C, 10 PZT layers could be fabricated. On the other hand, on the sample with a Pt thickness of 1 µm and deposition at room temperature (RT), stable PZT layers could not be fabricated because the sample was destroyed after the second layer was added.

Figure 9 shows the displacement distribution of the Pt layer measured before deposition of the PZT thin film. The Pt layer had tensile stress caused by the 200°C deposition and compressive stress caused by the RT deposition. Therefore, at different deposition temperatures, the stress was found to have reversed tension and compression. Thus the stress of the Pt layer was inversed, and stable fabrication became possible.

A PZT thin film generally exhibits tensile stress and the Pt layer fabricated under a heated condition has the same tensile stress. We think that matching the stress direction causes the stress relaxation of the capacitor.

Figure 10 shows the temperature dependence of the Pt layer stress on a releasable substrate. As the temperature changed, the direction of the Pt film stress changed gradually. By changing the deposition temperature, compressive stress changed to tensile stress. Therefore in order to obtain a tensile stress, heating to more than 200°C is required. Therefore stable fabrication of PZT film requires at least 200°C.

4.1.2 Thin film structure

Figure 11 shows the XRD patterns of the fabricated PZT thin films.

The XRD analysis revealed the intense peak of (110) orientation that was the PZT perovskite structure. After the 10th PZT layer was fabricated, the (110) peak intensity became higher.
4.1.3 Electrical properties

Figure 12 shows an example of the hysteresis loop. This loop shape was common to all the samples. Dielectric constants were about 1,300 in all capacitors, and dependency on the deposition condition (Pt layer thickness and deposition temperature) was not observed. It was found that the electrical characteristics do not depend on the deposition condition of Pt layer.

The electrical characteristics of capacitors fabricated on a releasable substrate were compared with those of conventional ones. Table 1 shows a comparison of the capacitors. Permittivity was not inferior to conventional capacitors. Remanent polarization was about the same as for conventional capacitors. The coercive field was larger than that of conventional capacitors, because the crystal structure is different from that of conventional capacitors. We confirmed that the capacitor on the releasable substrate had 110 orientation. However it is well known that a conventional capacitor has 100 orientation. Generally, a capacitor which has 100 orientation shows high electrical properties. So it is possible to equal this by improvement of the film quality.

That is, it is expected that the electrical characteristics can be improved by changing the crystal orientation.

4.1.4 Releasing properties

The releasing properties of the SiO$_2$-Pt interface were investigated using the tape peeling test.

From the tape test results, as shown in Fig. 13, we found that the release properties could be divided into three types: the capacitor could be peeled off completely, the capacitor could be peeled off partially, and the capacitor could not be peeled off.[3]

The Pt thickness and PZT thickness are used as parameters in Fig. 13. The gray area is the region where peeling is expected to occur. In the sample with the non-peeling area, the PZT was firmly adhered at the SiO$_2$-Pt interface, and also did not peel off by any means other than by tape.

As seen in Fig. 13, the thicker the Pt layer, the more easily the film releases. The possible reason for this result may be that the adhesion between the SiO$_2$-Pt was weakened by the thickness of the Pt layer which had greater stress, thus the capacitor became easier to peel.

On the other hand, the capacitor cannot be peeled off when the PZT is thicker. We think that the reason for this is diffusion at SiO$_2$-Pt interface. Increasing the number of thermal processes caused diffusion and made it impossible to release.

4.2 BaTiO$_3$ (EXP-2)

4.2.1 Results and discussion of Exp-2-1

All 9 variations of the BaTiO$_3$ samples shown in Fig. 6 were prepared without destruction in the formation process. The appearance of the prepared samples is shown in Fig. 6. A patterned Ti layer is useful for protecting the crystallization from destruction during the heat treatment. The film thickness of the prepared samples ranged from 1.0 to 1.2 mm. The dielectric constant of the BaTiO$_3$ films ranged from 300 to 600, which is almost the same as that which has previously been reported. The results are sum-
A perovskite structure was confirmed in the crystal structure by an XRD analysis, as shown in Fig. 14. Figure 14 shows that the orientation is the (110) preferred in this experiment.

Figure 15 shows that the coated film on the Pt lower electrode could not be crystallized and that the structure was destroyed. On the other hand, the film coated on the Pt/Ti lower electrode was crystallized without destruction.

Table 2  Summary of experimental results of BaTiO₃.

<table>
<thead>
<tr>
<th>Pattern</th>
<th>Size</th>
<th>Film fabrication</th>
<th>Film thickness</th>
<th>εᵣ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Circle</td>
<td>16 mm</td>
<td>○</td>
<td>1.1 µm</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>14 mm</td>
<td>○</td>
<td>1.2 µm</td>
<td>360</td>
</tr>
<tr>
<td></td>
<td>12 mm</td>
<td>○</td>
<td>1.0 µm</td>
<td>480</td>
</tr>
<tr>
<td>Square with rounded corner</td>
<td>16 mm</td>
<td>○</td>
<td>1.2 µm</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>14 mm</td>
<td>○</td>
<td>1.2 µm</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>12 mm</td>
<td>○</td>
<td>1.3 µm</td>
<td>490</td>
</tr>
<tr>
<td>Square</td>
<td>16 mm</td>
<td>○</td>
<td>1.2 µm</td>
<td>570</td>
</tr>
<tr>
<td></td>
<td>14 mm</td>
<td>○</td>
<td>1.4 µm</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td>12 mm</td>
<td>○</td>
<td>1.4 µm</td>
<td>540</td>
</tr>
<tr>
<td>Without pattern (Pt, 200°C)</td>
<td>×</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Without pattern (Pt, RT)</td>
<td>×</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Without pattern (Ti/Pt)</td>
<td>○</td>
<td>1.2 µm</td>
<td>650</td>
<td></td>
</tr>
</tbody>
</table>

A tape test was performed to evaluate the release of the prepared capacitors from the substrate. No capacitor was released from the substrate of the lower electrode with the Ti layer. The capacitors were easily released from the Pt/Ti electrode. These results show that the Ti layer has a strong bonding force between the substrate and the capacitors. In the previous study, almost the same process was carried out as expected and into the destruction and/or release during the process. These results show that there is an optimum design of the Ti layer of the lower electrode for successful use of the nano-transfer method. A patterned Ti layer is effective for this proposed process.

4.2.2 Results and discussion of Exp-2-2

The No. ① sample shown in Fig. 16 was crystallized successfully in the preparation process without destruction. The No. ② and ③ samples were partially crystallized; the area of the Pt/Ti electrode was successful but the part with only Pt was partially destroyed. This destruction was partial and was different from the total destruction shown in Fig. 16. Local destruction on the Pt layer only was observed. Uniform crystallization was achieved for the No. ④ sample without destruction.

Although the areas of the No. ② and ③ samples are the same as that of the No. ① sample and some of the samples in EXP-2-1, the structure was destroyed during crystallization. This shows the effectiveness of the Ti layer at the corner area for protecting against destruction during the crystallization process.

On the other hand, this was not the case for the No. ④ sample in spite of the location of the Ti. The No. ④ sample was not destroyed during crystallization. This might have occurred for the following reasons: 1) the large area of the Ti layer or 2) damage caused by heat treatment repeated over ten times. The design of the electrode also has different symmetry from the samples in EXP-2-1. Protection from destruction could have been caused by the large Ti layer having a strong bonding force between the wafer and lower electrode even in a low-symmetry design. Repeated heat treatments would lead to the diffusion of the Ti in the larger volume of the film structure.
5. Conclusions

We investigated the correlation between the releasing properties and fabrication conditions in the nano-transfer method. We found that by changing the deposition conditions and thickness of the Pt layer to control and change the stress, stable fabrication of a PZT capacitor is possible. Therefore, substrate heating during Pt sputtering is effective to fabricate the PZT films for this study. We evaluated the characteristics of the capacitors, and confirmed that the performance meets the basic requirements. Also, we investigated the correlation of the thickness and releasing characteristics and obtained basic knowledge for future application.

Lead-free ferroelectric thin films were prepared on a releasable substrate as an investigation of chip production. The process flow of the film preparation was established as expected. This will lead to development of a packaging technique for polymer substrates.

The formed films have the random orientation of a perovskite structure and a dielectric constant of about 650. This indicates that these thin films have adequate characteristics and crystal structures to provide improved performance. The main focus of this study is the film preparation using lead-free dielectric BaTiO₃. It will be possible for this process technology to be applied to other ferroelectrics, including Pb.

Acknowledgement

We would like to show our appreciation for Mr. I. Terada and Mr. M. Obata for their assistance in the preparation of the samples and Ms. T. Tanaka for the preparation of the manuscript of this article.

References


