1. Introduction

Piezoelectric materials and shape memory alloys (SMA) are widely used for actuator and sensor applications [1,2]. It is well known that piezoelectric materials produce an electric field when the stress is applied, while it shows deformation when the electric field is applied. The response time of piezoelectricity is relatively fast, but the displacement of that is relatively small comparing to the other actuators. Shape memory alloys, on the other hand, can produce a large force-displacement during martensite-to-austenite transformation. However, the response time of shape memory effect is slow comparing to that of piezoelectricity, because the shape memory kinetics are controlled by the thermal diffusivity.

Combination of piezoelectric materials with shape memory alloys and formation of the heterostructure are expected to fabricate the advanced materials which show integrated function of piezoelectricity and shape memory property with keeping the function of each material [3,4]. If the heterostructure of shape memory (TiNi) film and ferroelectric film is heated at the martensite-austenite transformation temperature, the large force-displacement occurred in the TiNi film layer is supposed to cause the change of electric field in the ferroelectric film layer. Therefore, the self detection of the displacement can be performed by monitoring the electromotive force, and the self detection function seems to be the integration of sensing and actuating function.

In order to obtain the smart material, it is necessary to design the heterostructure film without losing the functions of each other by means of chemical interaction at the interface. The PZT films were prepared by sol-gel process, and the TiNi films were deposited on PZT films heated at elevated temperatures. On growing the heterostructures, lowering the crystallization temperature of TiNi film plays an important role in achieving the heterostructure without inter-diffusion. In this study, we describe the depositing process of heterostructures. In conjunction with the heterostructures, lowering the crystallization temperature of TiNi film was also investigated in term of the surface morphology, and the ferroelectric properties of the PZT layer were measured.

2. Experimental Procedure

To prepare the piezoelectric film layer, commercially supplied PZT(52/48) precursor solutions were used. (Kanto Chemical Co.) Partially hydrolyzed 0.5 M precursors were deposited onto Pt/Ti/SiO$_2$/Si substrates with a spin coater operated at 3000 rpm for 40 sec. Pt/Ti electrode layer of the substrate was...
prepared by RF magnetron sputtering. The sequence of spin coating, drying at room temperature and pyrolysis at 450°C for 3 minutes was repeated ten times. Finally, the precursor films were fired at 700°C for 1 minute in O₂ atmosphere. The firing temperature at 700°C was determined by the results of the former report for PbTiO₃ type ferroelectric films [5]. The thickness of fired films determined by SEM micrographs were 0.8 μm.

1 μm-thick TiNi thin films were deposited onto PZT/Pt/Ti/SiO₂/Si and Pt/PZT/Pt/Ti/SiO₂/Si substrate by RF magnetron sputtering with the alloy target (Ti₅₂Ni₄₈). The crystallization temperature of the TiNi film was examined by varying the substrate temperature between 250°C to 550°C in increments of 100°C.

The crystal structures were examined with the X-ray diffractometer (XRD) and the microstructures were observed with a scanning electron microscopy (SEM). The surface morphologies of the TiNi films were observed by an atomic force microscope (AFM). The capacitances of the PZT films were measured with a 10 mV signal at 10 kHz using a digital LCR meter to calculate the dielectric constant. The ferroelectric properties of the PZT films were examined through the analysis of the P-E hysteresis curves using a ferroelectric test system (RT66A: Radiant Technology).

3. Results and Discussion

3-1. Preparation of Heterostructure without Chemical Interaction

Figure 1(a) shows the XRD result of the PZT/Pt/Ti/SiO₂/Si film fired at 700°C for 1 min. All peaks are corresponded to the perovskite peaks except for Pt peak, so that this film showed a well-defined perovskite single structure with the random orientation. TiNi film was directly deposited onto the PZT/Pt/Ti/SiO₂/Si substrate heated at 550°C by sputtering process. The XRD result obtained from TiNi/PZT/Pt/Ti/SiO₂/Si film was shown in Fig. 1(b). From this result, the crystal structure of TiNi was determined to B2 cubic austenite phase. Beside the presence of the perovskite phase of PZT and the B2 (110) phase of TiNi, furthermore, Ni-rich compound such as Ti₆Ni₁₄ or TiNi₃ were observed. The result
indicates the chemical interaction took place at the interface between PZT and TiNi layer. This chemical interaction is supposed to be the reaction of titanium and oxygen because the affinity of titanium for oxygen is higher than that of Pb, Zr and Ni. It is thought, therefore, that the oxygen in the PZT layer diffuse to the TiNi layer and react with Ti atoms. As a result of the reaction, Ni-rich compounds were considered to occur in the TiNi layer. To avoid the diffusion and reaction of oxygen, we inserted Pt layer as the diffusion barrier between TiNi and PZT layer because Pt can act as the diffusion barrier for PbTiO₃ type ferroelectric layers. Figure 1(c) shows the XRD result of the TiNi film deposited on Pt/PZT/Pt/Ti/SiO₂/Si substrate at 550°C. Despite inserting the Pt layer with 0.2 μm thickness, it can be seen from this figure that the residual peak of Ni-rich compound was found. This result suggests that the Pt layer is not sufficient to prevent the diffusion at 550°C. The inter-diffusion through the Pt layer can be suppressed at lower deposition temperature. TiNi films, therefore, were deposited on the Pt/PZT/Pt/Ti/SiO₂/Si and the PZT/Pt/Ti/SiO₂/Si substrates at 350°C, and XRD results are shown in Fig. 2.

For the TiNi film deposited on PZT/Pt/Ti/SiO₂/Si substrate, as shown in Fig. 2(a), any peaks except for Pt(111) and Si(100) peaks was not found, so that TiNi layer was shown to exhibit amorphous structure. In Fig. 2(b), it can be seen that the XRD pattern consists of the perovskite peaks of PZT, B2(110) peak of TiNi, Pt(111) peak and Si(100) peak, and any peaks associated with the chemical interaction as shown in Fig. 1(b, c) were not observed. This results exhibit that the sputter deposition of TiNi onto Pt layer promote the (110) oriented texture and lower the crystallization temperature of the TiNi film comparing with the reported crystallization temperature which is about 500°C [6].

Figure 3 shows the cross-sectional SEM micrograph of TiNi film deposited on Pt/PZT/Pt/Ti/SiO₂/Si substrate at 350°C. The micrograph shows clear interface between TiNi, Pt and PZT layer, and any other inter-diffusion layers can not be observed. Therefore, we can succeed to fabricate the heterostructure of TiNi and PZT layer without chemical interaction at the interface by lowering the crystallization temperature of TiNi film using the Pt under layer.
3.2. Lowering the Crystallization Temperature of TiNi Film

Figure 4 shows the XRD profiles of the TiNi thin films deposited on the SiO$_2$/Si and the Pt/SiO$_2$/Si substrate at 350°C. The same behaviour with the result in Fig. 2 was obtained. TiNi film on the SiO$_2$ surface exhibits the amorphous structure, while film with a (110) oriented plane was crystallized on the Pt surface heated above 350°C. The results indicated in Fig. 2 and Fig. 4 suggest that the surface features affect the crystallization process of TiNi films during deposition. In order to investigate the process of TiNi coverage, the surface morphology of the TiNi thin films was observed by AFM.

Figure 5 shows the surface morphology of the 100 nm-thick-TiNi films deposited on SiO$_2$/Si at 350°C (a) and Pt/SiO$_2$/Si at 350°C (b). The differences are observed in the morphologies of TiNi films. The TiNi film on the Pt surface shows many islands, while the TiNi film on the SiO$_2$ surface is smooth. The surface roughness factor, $R_a$, calculated from images obtained by AFM was indicated in Table. 1 with the results of substrates. The mean roughness, $R_a$, of the TiNi film deposited on SiO$_2$/Si substrate are almost consistent with the result of the SiO$_2$/Si substrate. This result suggest that Ti-Ni atoms just deposited on the substrates without any particular arrangement of atoms.

Figure 4. XRD results of (a) TiNi deposited on the SiO$_2$/Si substrate at 350°C and (b) TiNi deposited on Pt(10 nm)/SiO$_2$/Si substrate at 350°C.
However, crystallization of the TiNi films occurred with the increase of surface roughness. Therefore, the crystallization of the TiNi film is closely related to an island growth mechanism. The elevated temperature increases the mobility of the adatoms and promotes surface diffusion. When an adatom collides with another adatom which is its nearest neighbor, both adatoms become immobile and form the TiNi crystalline nuclei. These nucleate grow and annex the surrounding condensed adatoms, and become an island. It is believed that the nucleation energy may be introduced by the thermal energy transformed from the adatom collision. The TiNi with (110)-orientation is considered to be related to the thermodynamic preference of initial island growth to the lower surface energy, because the (110) plane has the lowest surface energy for a bcc structure.

However, the deposition of TiNi films on the SiO$_2$/Si and PZT/Pt/Ti/SiO$_2$/Si substrates has no effect on lowering the crystallization temperature. This result can not be explained by the adatom surface mobility, although the surface of the Si oxide substrate is smoother than that of the Pt/Si oxide/Si substrate. In this case, we can consider that the Ti-O interfacial adsorption acts as the nucleation barrier, because the adsorption energy of titanium on the oxide substrate is higher than that of nickel [7]. Titanium atoms attracted to the oxygen site in the Si oxide surface hinder the surface adatom mobility, and thus, the surface mobility is insufficient to generate crystalline nuclei.

### 3-3. Ferroelectric Properties

Finally, ferroelectric properties of the heterostructures, TiNi deposited on PZT/Pt/Ti/SiO$_2$/Si at 550°C and TiNi deposited on Pt/PZT/Pt/Ti/SiO$_2$/Si at 350°C, films were measured. The TiNi and TiNi/Pt layer as the top electrode of PZT was sputtered through a 0.5 mm diameter shadow mask on the PZT/Pt/Ti/SiO$_2$/Si film with a same sputtering condition described in Fig. 2. Figure 6 shows the P-E hysteresis curve of the heterostructure films at an applied field of 225 kV/cm. The P-E hysteresis curve of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ra (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$(300 nm)/Si</td>
<td>0.12</td>
</tr>
<tr>
<td>TiNi(100 nm) deposited on SiO$_2$(300 nm)/Si at 350°C</td>
<td>0.12</td>
</tr>
<tr>
<td>Pt(10 nm)/SiO$_2$/Si</td>
<td>0.2</td>
</tr>
<tr>
<td>TiNi(100 nm) deposited on Pt(10 nm)/SiO$_2$/Si at 350°C</td>
<td>0.4</td>
</tr>
</tbody>
</table>
TiNi/PZT/Pt/Ti/SiO2/Si film in Fig. 6(a) exhibits a parabolic shape as it approaches the maximum coercive field values. This feature is likely a result of the leakage current which is associated with the inter-diffusion between the TiNi and PZT layer. On the other hand, TiNi/Pt/PZT/Pt/Ti/SiO2/Si film in Fig. 6(b) showed the ferroelectric behaviour, and Pr and Ec determined by the P-E hysteresis curve were 16 μC/cm², and 67 kV/cm, respectively, and these value is similar with those of the single PZT film [8].

4. Conclusion

To integrate functions of shape memory and ferroelectricity, the deposition condition and the crystalline phase for the heterostructure of the sputtered TiNi and sol-gel derived PZT are investigated. The oriented Pt layer, which decrease the crystallization temperature of TiNi layer to 350°C, at the interface between TiNi and PZT. The cross-sectional SEM micrograph showed clear interface for each layer and did not show inter-diffusion layer. This heterostructure, TiNi/Pt/PZT/Pt/Ti/SiO2/Si, film indicated the B2(110) phase of TiNi and the perovskite phase of PZT. PZT layer showed the ferroelectric behaviour, and Pr and Ec determined by the P-E hysteresis curve were 16 μC/cm² and 67 kV/cm, respectively.

Further investigations of the shape memory effect in TiNi layer and the transformation characteristics through the interface are needed to exert the heterostructure film as the integrated function materials.

References