Effect of Mn Substitution on Structural, Microstructural, Nonvolatile Memory and Switching Behaviour of Bi$_4$Ti$_3$O$_{12}$ Thin Films

May Aye Khaing$^1$, Than Than Win$^2$, Yin Maung Maung$^2$, Win Win Thar$^3$ and Ko Ko Kyaw Soe$^4$

Abstract
Manganese (Mn) doped Bismuth Titanate (Bi$_x$Ti$_3$O$_{12}$) powders (BMT) were prepared by solid state mixed oxide route and annealed at 1000°C to become polycrystalline powders. Bi$_4$Mn$_x$Ti$_{3-x}$O$_{12}$/n-Si ($x$ = 0.0, 0.1, 0.2, 0.3 and 0.4) thin films were also prepared by own sol-based method, spray pyrolysis coating techniques and heat treated at 600°C. X-ray diffraction (XRD) investigation was carried out to examine the structural properties of BMT powder. The microstructural characteristics of the films were determined by Scanning Electron Microscope (SEM) spectroscopy. For the ferroelectric characterization and non-volatile memory effect, 100 kHz and 10 V thermal hysteresis loop were observed by Sawyer-Tower circuit. The composition dependence of the transient current characteristic in the sample had been studied by I-t measurement in the different frequencies. From the experimental results the transient switching time was faster and faster with increasing Mn compositions.

Key words: BMT, XRD, SEM, hysteresis, Sawyer-Tower

Introduction
Ferroelectricity in Bi$_4$Ti$_3$O$_{12}$, also known as BIT, was described by Subbarao (1961) and Van Uitert (1961) in parallel works, and few year later Cummings (1968) described the monoclinic symmetry and polar domain structure in BIT. After these initial works, the best known compound within the Aurivillius family, Bi$_4$Ti$_3$O$_{12}$, an attractive lead-free substitute for the materials commonly used in ferroelectric random access memory (FeRAM), and its crystal structure and ferroelectric properties have been extensively studied. Nowadays, due to its large remanent polarization ($P_r$), low crystallization temperature and high Curie temperature, more than 70 compounds of this family were known and more than 50 present ferroelectricity (Herbert, 1982). Ion substitution in the BIT is known to be an effective technique for improving its electrical properties, such as $P_r$ and fatigue characteristics (Zhong et al, 2008). Moreover the switchable diode effect means that the polarity of the diode can be reproducibly switched by the reversion of the applied electric field in the MFM structures, due to the polarization modulated barrier (Chon Ge el al., 2013). Most interestingly, the switchable diode effect has been demonstrated recently in various ferroelectric structures ranging from organic films (Asadi et al, 2008), inorganic bulks (Choi, 2009), and inorganic films (Yang, 2009). In the present study, manganese (Mn) doped bismuth titanate (Bi$_4$Ti$_3$O$_{12}$) thin films were prepared by a solid-state reaction technique. The effect of manganese on growth and characteristics of bismuth titanate thin films was investigated.

Experimental
Preparation of BMT powder
Bismuth Manganese Titanate (abbreviated to BMT) powders with a stoichiometric composition Bi$_4$Mn$_x$Ti$_{3-x}$O$_{12}$, ($x$ = 0.0, 0.1, 0.2, 0.3, 0.4) were prepared by solid-state mixed oxide route. The starting materials used were Bi$_2$O$_3$ (with purity 100%), MnO$_2$ (with purity 96.756%) and TiO$_2$ (with purity 98.209%) analyzed by XRD spectroscopy. The powder was weighted on electronic balance (FEJ-200) to agree molar ratio with the composition of

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Bi$_4$Mn$_x$Ti$_{3-x}$O$_{12}$ ($x = 0.0$ to $0.4$) and it was mixed in a cleaned agate mortar and ground with a pestle for 3 hours each to form homogeneous. Later, sieve it with a mesh to become uniform grain size. The mixtures of each powder was then placed in the cleaned-crucibles and heat-treated at 1000°C for 2 hours in air atmosphere with method of solid state mixed oxide route. In addition, these samples were ground in a cleaned agate mortar and sieve them with a mesh secondly to be good fined powder.

The n-type Silicon Cleaning Sequence

The n-type silicon wafers (1cm×1cm×0.0625cm) were washed in boiling acetone (60°C), then in boiled propanol (50°C) for 5 minutes to remove greasy films and organic impurities. They were immersed in nitric acid (HNO$_3$) for 3 minutes in order to remove ionic contaminations. To avoid the functional defects, they were etched by the buffered hydrofluoric acid (34% of NH$_4$F: 6.8% of HF: 58.6% of H$_2$O) for 2 minutes. Then, the substrates were rinsed in deionized distilled water and dried on flat oven at 100°C in open air for a few minutes.

Preparation on Precursor Solution of BMT

For a polymerizable solution system, Bi, Ti and Mn required choosing solvents and metallo organic sources. Powders of Mn doped bismuth titanate (BTO), the solvents 2-methoxyethanol and glacial acetic acid were selected based on their successful application. Bismuth oxide (Bi$_2$O$_3$) is not soluble in alcohol such as in 2-methoxyethanol but dissolved in glacial acetic acid above 70°C. So, to become less sediment, two grams of sample powders were added into 8 drops, 10 drops, 12 drops, 14 drops and 16 drops of glacial acetic acid with respect to dopant concentration respectively. And then pour 10ml of 2-methoxyethanol to the mixture and stirring the solution with a small glass ladle. The getting solution was refluxed in steel-container of oil-bath at the boiling point 100°C. Finally BMT precursor solution was obtained.

BMT Thin Film Fabrication Process (Spray Pyrolysis)

The prepared precursor solution was deposited on the n-Si substrate by using spray pyrolysis process. The silicon substrate was set up on the holder of the spray target heating 200°C. The distance between substrate and the nozzle of the pressure gun was 15.5 cm long and the diameter of the nozzle was 0.3 mm wide. The inclination angle of the substrate holder which affect evidently on grain size and thickness of film, was set up (45°) to the nozzle of the pressure gun. Before the experimental research, according to the fore testing machine, the inclination angles with increasing (0°), (15°), (30°) cause affectively decreasing grain sizes and thickness but increasing with many of pores in the surface of the film. In this process, the reason that substrate holder was fixed temperature at 200°C, was to absorb the precursor more. The container of the spray machine was filled with the ambient air compressed about 30 psi (pound square inch) manually controlled. The preparation of BMT / n-Si thin film was performed according to the above situation. After the deposition, the layers of coating were firstly spin-dried at room temperature in N$_2$ atmosphere and then annealed at 600°C for 1 hour. Then, the Schottky barrier and Ohmic contact were set up on the junction diode as thin film device. Finally, Bi$_4$Mn$_x$Ti$_{3-x}$O$_{12}$ / n-Si thin films were achieved as ‘metal-BMT / n-Si-metal’ devices.

Results

Structural Properties

X-ray diffraction (XRD) carried out the sample to investigation phase assignment and lattice parameters as illustrated in Figure 1. The samples were scanned from 10° to 70° in 20
with a step size of 0.01. The sizes of Mn-doped BTO polycrystalline powders oriented along (hkl) plane could be deduced from well-known Debye Scherrer’s formula,

\[ d(hkl) = \frac{0.98 \lambda}{\beta \cos \theta} \]

where \( \lambda \) was the wavelength of incident X-ray radiation (1.54056 Å), \( \beta \) was the broadening of diffraction line measured at half of its maximum intensity in radians (FWHM) and \( \theta \) was the Bragg’s diffraction angle corresponding to the (hkl) peak. Crystallite sizes were observed in Table 1. From XRD analysis, lattice parameters and structural parameters were evaluated. The lattice parameters of the Mn-doped Bi\(_4\)Ti\(_3\)O\(_{12}\) were slightly different from pure Bi\(_4\)Ti\(_3\)O\(_{12}\). It may be due to Mn ions partially occupied by Ti site in Bi\(_4\)Ti\(_3\)O\(_{12}\).

Table 1. Lattice parameters of Mn doped BTO powders

<table>
<thead>
<tr>
<th>Mn doped BTO powder</th>
<th>a (Å)</th>
<th>B (Å)</th>
<th>C (Å)</th>
<th>FWHM of (117) plane (rad)</th>
<th>Crystallite size of (117) plane (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X=0.0</td>
<td>5.4504</td>
<td>5.4281</td>
<td>32.6284</td>
<td>2.408E-3</td>
<td>649</td>
</tr>
<tr>
<td>X=0.1</td>
<td>5.4573</td>
<td>5.4168</td>
<td>32.9278</td>
<td>3.612E-3</td>
<td>432</td>
</tr>
<tr>
<td>X=0.2</td>
<td>5.3758</td>
<td>5.4049</td>
<td>32.6908</td>
<td>3.577E-3</td>
<td>437</td>
</tr>
<tr>
<td>X=0.3</td>
<td>5.4221</td>
<td>5.2951</td>
<td>32.7332</td>
<td>4.014E-3</td>
<td>392</td>
</tr>
<tr>
<td>X=0.4</td>
<td>5.4202</td>
<td>5.3406</td>
<td>32.3296</td>
<td>3.700E-3</td>
<td>425</td>
</tr>
</tbody>
</table>

Microstructural Properties

The surface morphology of Bi\(_4\)Mn\(_{x}\)Ti\(_{3-x}\)O\(_{12}\) / n-Si thin film was studied by Scanning Electron Microscopy (SEM) and illustrated by Figure 2 and Figure 3. These films showed different morphology of surfaces grains, which were depended on different contents of the added acetic acid drops to the sample. The surfaces of all films were generally non-uniform and fairly dense. And also, there were existences of some pores on the films’ surfaces but without cracking. These facts indicate that the pores in the surfaces were related to the decomposition relation of the precursor solution and the evaporation of residual organic in these films. The becoming uniform and less pores with the smaller grain size have been getting in sample (x = 0.4) by adding 16 drops (0.8 ml) of acetic acid. The grains of the surfaces that become smaller for each sample with more dopant concentration were 4 µm, 3 µm, 2.7 µm, 2 µm and 1.5 µm.
long respectively. And, the values of thickness for each sample were 6.3 µm, 5.0 µm, 4.7 µm, 4.3 µm and 4.7 µm.

Figure 2. SEM of films with different dopant concentration (x = 0.0 to 0.4) by adding gradually more contents of acetic acid and uncoated n-type silicon

Figure 3. SEM of films’ thickness with different dopant concentration (x = 0.0 to 0.4) by adding gradually more contents of acetic acid

**P-E Hysteresis Measurement**

To measure ferroelectric properties, the Cu-BMT-Cu sample was placed in the sample holder. A triangular derived voltage signal was applied to the basic Sawyar-Tower circuit. To be \( V_{\text{rms}} = 1 \text{V}, V_0 = 1.4142 \) and peak to peak voltage signal must be 2.8284V as a standard voltage because the more voltage applies, the more current loses. Applied frequency 10 kHz was a fined resonance situation for all samples, as to be a standard resonance frequency, the variable resistor had to be aimed justly in harmony due to frequency which was inversely proportional to the resistance in RC series circuit.

The value of variable resistor was 100 kΩ. But frequency 10 kHz and 9.7776 kΩ match up. The linear sense capacitor used in the circuit was 1015 pF. The value of remanent polarization \( P_r \), spontaneous polarization \( P_s \), and coercive field \( E_c \) could be counted in the screen of the oscilloscope.

It can be deduced from the Figure 4 that ferroelectric hysteresis loops were changed with respect to stoichiometric compositions. In addition, the good symmetrical polarizations of the samples were getting and the \( P_r, P_s \) value of BMT (x = 0.3) and (x = 0.4) were higher than others in the smaller value of electric field \( E_c \). So, the values of \( P_r \) and \( P_s \) were going to be studied with different applied electric field. When the field was reduced below \( E_c \), the loop shrinked, and it became a narrow ellipse beak with its major axis parallel to the almost horizontal portion of the fully developed loop. The hysteresis loop of BMT samples varied according to compositions and structures.
I-t Characteristic of BMT / n-Si Thin Film Device

The slow switching process was of great interest for the application in access memories, since it could limit the access time of the memory cell at low operating voltage. BMT / n-Si thin films with dopant concentration (x = 0.0 ~ 0.4) had attached much attention for application in memory devices like dynamic random access memories (DRAM) and non-volatile memories. The composition dependence of the transient current characteristic in the ferroelectric thin film had been studied by I-t measurement in the different frequencies. I-t characteristics were measured at room temperature and various frequencies using the simple C-R circuit as a differentiator with the oscilloscope (YOKOGAWA ALS10) and signal generator (Griffin). At applied voltage range from 0.75 V to 1 V, the transient current of Mn doped Bi$_4$Ti$_3$O$_{12}$ deposited on n-type silicon thin films were measured at frequency range from 1 kHz to 100 kHz.

The current versus time (I-t) characteristics consists of two components the electric conduction current and the polarization current. The trapped holes caused increasing of the local electric field and the conduction current. Because the trapping of charge carriers was a function of temperature due to the alternately change applied electric field. The transient current at low stress voltage was mostly due to the polarization current. The decreasing transient current behavior at low stress voltage was designed as "polarization type". The transition between the two different regions was called the transition voltage. The polarization current decreases and saturates as time increase. The conduction current increases and saturates as time increase.

The dependence of transient current on temperature relied on the relative magnitude of two components, current, I and time, t. When the spontaneous polarization reverse a displacement current to flow in the resistor, the current I could be displayed on an oscilloscope as a function of time "t". The current due to reversal of the polarization was called the switching current or the transient current. The transient current for charging and discharging were determined by measuring the voltage drops through the resistor. Depending on the relative magnitude of the current components, the transient current characteristic could be separated into two different types, the degradation type and the polarization type. The transient current increases with time in degradation type region and decreases exponentially with time in the polarization type region.

The transient current nature types of Bi$_4$Mn$_x$Ti$_{3-x}$O$_{12}$ / n-Si devices with Cupper, Cu electrode, were polarization transient types and exponentially decay with time taken to switch. The maximum switching transient current ($i_{max}$) and switching time ($t_s$) of BMT / n-Si devices are revealed in Table 2. The transient switching time of the Bi$_4$Mn$_{0.4}$Ti$_{2.6}$O$_{12}$ / n-Si device in 1 V input voltage is faster than that of the other samples especially Bi$_4$Mn$_{0.3}$Ti$_{2.7}$O$_{12}$ / n-Si device as illustrated in Figure 5. This effect could be explained that an internal field originated from some kinds of space charges which were redistributed to compensate for the residual depolarization field.
Table 2. Electrical parameters derived from the analysis of I-t characteristic for BMT / n-Si thin films with Mn composition (x = 0.0 ~ 0.4)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>x=0.0</th>
<th>x=0.1</th>
<th>x=0.2</th>
<th>x=0.3</th>
<th>x=0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{\text{max}}$ (1 V)</td>
<td>1.64</td>
<td>1.60</td>
<td>1.51</td>
<td>1.46</td>
<td>1.16</td>
</tr>
<tr>
<td>(x 10^-6 A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_s$ (1 V)</td>
<td>5.626</td>
<td>5.272</td>
<td>4.574</td>
<td>4.230</td>
<td>3.876</td>
</tr>
<tr>
<td>(x 10^-4 sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$i_{\text{max}}$ (0.75 V)</td>
<td>1.20</td>
<td>1.15</td>
<td>1.10</td>
<td>1.07</td>
<td>0.88</td>
</tr>
<tr>
<td>(x 10^-6 A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$t_s$ (0.75 V)</td>
<td>4.522</td>
<td>4.834</td>
<td>4.562</td>
<td>4.426</td>
<td>4.240</td>
</tr>
<tr>
<td>(x 10^-4 sec)</td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

Conclusion

We synthesized polycrystalline Mn doped Bi$_4$Ti$_3$O$_{12}$ specimens using a solid-state reaction method with different concentrations of Mn ions (x=0.0, 0.1, 0.2, 0.3 and 0.4) in Bi$_4$Ti$_3$O$_{12}$. From XRD analysis, the lattice parameters of the Mn doped Bi$_4$Ti$_3$O$_{12}$ were slightly different with pure Bi$_4$Ti$_3$O$_{12}$. It might be due to Mn$^{4+}$ ions were partially occupied into Ti$^{4+}$ site in Bi$_4$Ti$_3$O$_{12}$. This was because of the formation of oxygen vacancy may appear for charge compensation in the crystal when Mn$^{4+}$ ion (ionic radius 0.530 Å) substitute at Ti$^{4+}$ (ionic radius 0.605 Å) site, which might also lead to the reduction of volume. From SEM analysis, the grain of the surface that become smaller and smaller for each sample with more dopant concentrations. Polarization properties of ferroelectric samples were assessed using P-E analysis. From the hysteresis loop measurement, BMT sample could be used as non-volatile ferroelectric random access memory. In the I-t measurement, the transient switching time of the Bi$_4$Mn$_{0.4}$Ti$_{2.6}$O$_{12}$/n-Si thin film device was faster than that of Bi$_4$Mn$_0$Ti$_{2.7}$O$_{12}$/n-Si thin film device and also faster and faster with internal energy is aligned in the same direction as the applied electric field. So, they could be pronounce switchable diode effect in ferroelectric diode. Thus, the present research allowed more economical coating, technical simplicity and easy adaptability. Moreover, the films fabricated with sol-based method were quite promising candidate for memory device applications.

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