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Microstructural and Electrical Properties of Mn Doped $Bi_4Ti_3O_{12}$ Thin Film Devices

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Abstract— Manganese (Mn) doped Bismuth Titanate ($Bi_4Ti_3O_{12}$) powders (BMT) were prepared by solid state mixed oxide route and annealed 1000°C to become polycrystalline powders. $Bi_4Mn_xTi_{(3-x)}O_{12}$ / n-Si (x= 0.0 to 0.4) thin films were also prepared by own sol-based method, spray pyrolysis coating techniques and heat treated at 600°C process temperature. The microstructural characteristics of the films were determined by Scanning Electron Microscope (SEM) spectroscopy. The density of state was determined from I-V characteristics and the switching behaveour has been studied by I-t characteristics. According to the results, the manganese composition (x=0.4) should be used in the ferroelectric memory applications rather than other compositions.

***Keywords*_** BMT, Ferroelectric, SEM, spray pyrolysis

1 Introduction

FERROELECTRIC materials are of characteristics to maintain the polarization state in the absence of a voltage and the possibility to reverse the polarization direction by applying an electric field [1]. It is an obvious idea to design robust nonvolatile random access memories based on intrinsic switchable ferroelectric polarization in the ferroelectric materials. Ferroelectric capacitive memories were regarded as a promising candidate for the next generation nonvolatile memories [2].

The polarization charges can affect the barrier at the interface between electrodes and ferroelectrics, and the reversal of the polarization produces a change in the band diagram [3]. As a result of this, bistable resistance states can be obtained for two opposite polarizations. In other words, the high and low resistance states stem from the interplay of polarization and conduction. Two ferroelectric resistive switching concepts are classified by the conduction mechanism [4]. 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. Most interestingly, the switchable diode effect has been demonstrated recently in various ferroelectric structures ranging from organic films, inorganic bulks , and inorganic films [5]. Structural, dielectric and ferroelectric properties of manganese (Mn) doped bismuth titanate ($Bi_4Ti_3O_{12}$) ceramics have been already reported [6]. In the present study, manganese (Mn) doped bismuth titanate ($Bi_4Ti_3O_{12}$) thin films are prepared by a solid-state reaction technique. The effect of manganese on the microstrual and electrical properties of bismuth titanate thin films is investigated.

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2 EXPERIMENTAL PROCEDURE

To prepare the colloidal precursor solution, Bi_2O_3, MnO_2 and TiO_2 were used as starting materials. Manganese (Mn) doped bismuyh titanate $Bi_4Ti_3O_{12}$ powder, the molar concentration of $Bi_4Mn_{(x)}Ti_{(3-x)}O_{12}$, (x = 0.0, 0.1, 0.2, 0.3, 0.4) were prepared by solid-state mixed oxide route. Which was described in previous paper [6]. Then BMT powder were weighed and mixed with 2-methoxyethanol and glacial acetic acid. Bismuth oxide (Bi_2O_3) was 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 10 ml of 2-methoxyethanol to the mixture and stirring the solution with a small glass ladle. The getting solution is refluxed in steel-container of oil-bath at 100°C and form precursor solution. The substrate used for this study was n-Si (100), which were (1 cm × 1 cm × 0.0625 cm). Before film fabrication, they were cleaned by silicon cleaning process [7,8]. Then the prepared precursor solution was deposited on the Si substrate by using spray pyrolysis process. After the deposition, the layer of coating were firstly spin-dried at room temperature in nitrogen 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.

3 RESULTS AND DISCUSSION

3.1 Surface Morphology of Thin Film

The surface morphology of $Bi_4Mn_{(x)}Ti_{(3-x)}O_{12}$ / n-Si thin film was studied by Scanning Electron Microscopy (SEM) illustrated by Fig (1). 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,

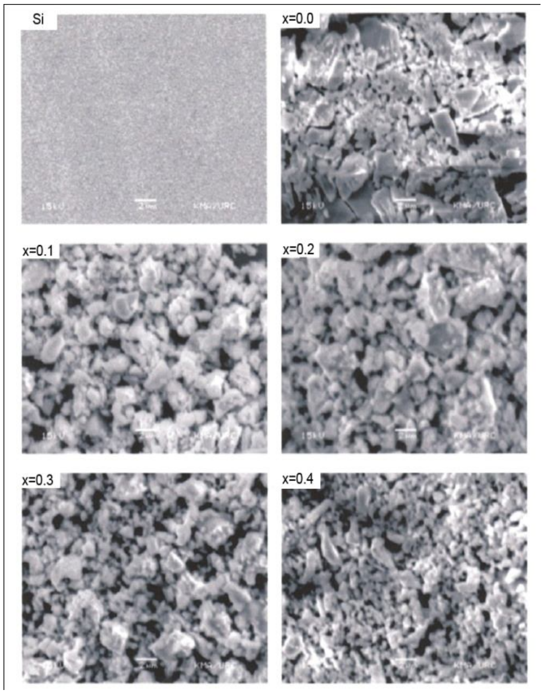

Fig. 1. SEM of films with different dopant concentration (x = 0.0 to 0.4) by adding gradually more contents of acetic acid and uncoated n-type silicon

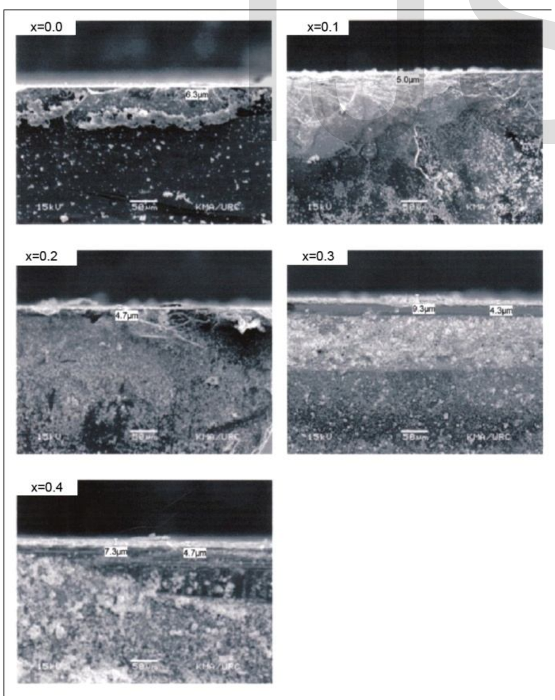

Fig. 2. SEM of films' thickness with different dopant concentration (x = 0.0 to 0.4) by adding gradually more contents of acetic acid

precursor solution and the evaporation of residual organic in these films. The becoming uniform and less pores with the smaller grain size had been getting in sample (x = 0.4) by adding 16 drops (0.8 ml) of acetic acid. The grains of the surfaces that became 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 6.3μm, 5.0μm, 4.7μm, 4.3μm and 4.7μm getting as shown in Fig 2.

3.2 I-V Characteristic of BMT / n-Si Thin Film Device

The current-voltage (I-V) characteristics for Cu - BMT / n-Si - Cu structure were obtained by using Digital Voltmeter (Wavetek) at room temperature. The samples were mounted on the copper holder stand and the electrical contacts were created with the upper electrodes by using silver paste. I-V characteristics were shown in Fig 3 and their data distribution were reported on Table 1. The saturation current, I_s for Mn composition x = 0.0 were found as 5.23 x 10^{-7}A and came down the value of I_s according to the more Mn content in the BMT oxide layer of the films.

In Mn composition (x = 0.4), the value of I_s was 1.16 x 10^{-9}A. Moreover, the values of the ideality factors were come close to unity gradually by bringing up the composition if 1.498 for sample (x = 0.4) especially compares to 1.903 for sample (x = 0.0). According to the saturation current, the barrier height, Φ_b^{I-V} could be obtained. The values of the barrier height, Φ_b^{I-V} were raised by the decreasing saturation current, I_s. The barrier height, Φ_b^{I-V} of a typical Cu - $Bi_4Mn_{0.4}Ti_{2.6}O_{12}$ / n-Si - Cu sample had 0.89eV.

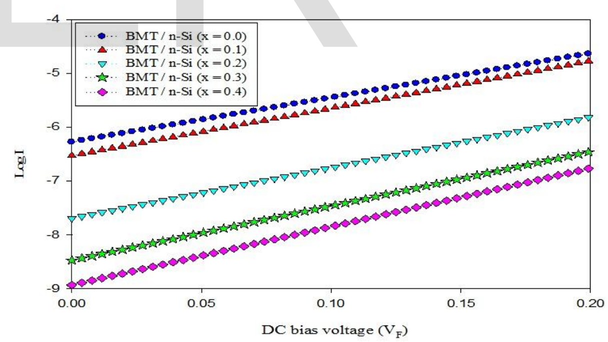

Fig. 3. Log I-V characteristics of BMT/n-Si thin film at composition (x=0.0~0.4)

Table 1. Electrical parameters derived from the analysis of I-V characteristic for BMT / n-Si thin films with Mn composition (x = 0.0 ~ 0.4)

Parameters	(x = 0.0)	(x = 0.1)	(x = 0.2)	(x = 0.3)	(x = 0.4)
I_s (A)	5.23x10^{-7}	2.95x10^{-7}	2.01 x10^{-8}	3.34x10^{-9}	1.16x10^{-9}
n	1.903	1.801	1.698	1.602	1.498
Φ_b^{I-V}(eV)	0.73	0.74	0.81	0.86	0.89

3.3 The Density of Interface State

The interface states energy distribution could be determined from the forward bias I-V measurement. This distribution could be obtained by taking into account the bias dependence of the ideality factor and barrier height. The higher value of the ideality factor, n was attributed to an order of magnitude higher density distribution of interface states. I-V curve was not ideal and the ideality factor was controlled by the interfacial states density. The evaluated density of interface states was a little higher than the value at the actual interface because the effect of series resistance, R_s had not been considered in the calculation of N_{ss}.

When the device was forward biased, the quasi-Fermi level for the majority carriers rises on the n-type semiconductor side. Thus, most of the electrons would be injected directly into the metal forming a thermionic emission current. While some of them were trapped by the interface states. This charge captures process results an increasing in the effective barrier height, thereby reducing the device current. As could be seen in Fig 4, N_{ss} decreases with increasing $E_c - E_{ss}$ (from mid gap towards the top of the conduction band). On the other hand, the increase of N_{ss} stems from mid gap towards the bottom of the conduction band. This increase was probably due to the increase of the series resistance R_s. The density distribution of the interface states changed in E_c range of 0.76 ~ 0.86eV and the value of N_{ss} was obtained 2.5919 x 10^{10}cm^{2}eV^{-1} at E_c = 0.76eV by using the I-V measurement for the typical Mn composition (x = 0.4) sample as described in Table 2.

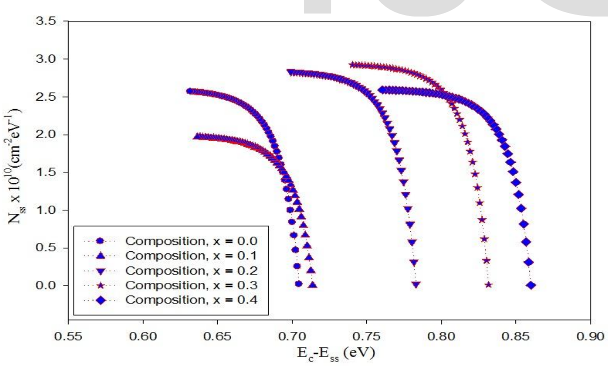

Fig. 4. Density of interface states as a function of Ec-Ess for BMT/n-Si (x=0.0~0.4) devices

3.4 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.

Table 2. Electrical parameters derived from the analysis of N_{ss}- (E_c – E_{ss}) characteristic for BMT / n-Si thin films with composition (x = 0.0 ~ 0.4)

Parameters	(x = 0.0)	(x=0.1)	(x=0.2)	(x= 0.3)	(x=0.4)
d (cm) x 10^{-4}	6.3	5.0	4.7	4.3	4.7
ε_{ox}	29.76ε_0	21.31ε_0	32.78ε_0	36.88ε_0	43.77ε_0
E_c-E_{ss}(max) (eV)	0.7049	0.7139	0.7831	0.8317	0.8601
N_{ss}(max) (x10^{10}cm^{2}eV^{-1})	2.5685	1.9699	2.8339	2.9235	2.5919
E_c-E_F (eV)	0.4920	0.4773	0.4702	0.4579	0.4563

The composition dependence of the transient current characteristic in the ferroelectric capacitors 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 BMT thin films were measured at frequency range from 1 kHz to 100 kHz.

The current versus time (I-t) characteristics consisted 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 decreased and saturated as time increase. The conduction current increased and saturated 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 reversed 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 increased with time in degradation type region and decreased exponentially with time in the polarization type region.

The transient current nature types of BMT films 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 were revealed in Table 3. The transient switching time of the BMT4 device in 1 V input voltage was faster than that of the other samples which were illustrated in Fig 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.

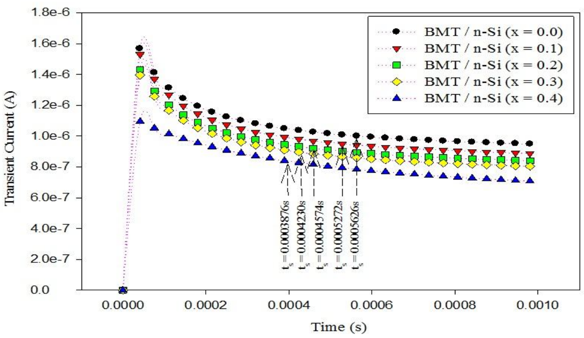

Fig. 5. The composition of transient current at switching (1)V

Table 3. Electrical parameters derived from the analysis of I-t characteristic for BMT / n-Si thin films with Mn composition (x = 0.0 ~ 0.4)

Parameters	***(x=0.0)***	***(x=0.1)***	***(x=0.2)***	***(x=0.3)***	***(x=0.4)***
i_{max} (1V) (x 10^{-6}A)	**1.64**	**1.60**	**1.51**	**1.46**	**1.16**
t_s (1 V) (x 10^{-4}sec)	**5.626**	**5.272**	**4.574**	**4.230**	**3.876**
i_{max} (0.75 V)(x 10^{-6}A)	**1.20**	**1.15**	**1.10**	**1.07**	**0.88**
t_s (0.75 V) (x 10^{-4}sec)	**4.522**	**4.834**	**4.562**	**4.426**	**4.240**

4 CONCLUSION

The metal-insulator (oxide)-semiconductor (MIS) diode was the most useful device in the study of semiconductor surfaces. Since, the reliability and stability of all the semiconductor devices were intimately related to their surface conditions, an understanding of surface physics with the help of MIS diodes was of great importance to device operation. The current conduction mechanisms across the devices were carried out using I-V measurements. The non-ideal forward bias I-V behavior observed in the Cu - BMT / n-Si - Cu devices were attributed to a change in the metal-semiconductor barrier height due to the interfacial layer, interface states, and the series resistance. The barrier height is an important parameter that determined the electrical characteristics of metal-semiconductor (MS) contacts.The saturation current is high in the $Bi_4Mn_{0.0}Ti_{3.0}O_{12}$ / n-Si device or BTO / n-Si sample compared with the $Bi_4Mn_{0.4}Ti_{2.6}O_{12}$ / n-Si device referred to BMT / n-Si (x = 0.4) sample. The bias dependent barrier height derived from the saturation current, though it was small, was considered for the determination of the interface state density distribution.Under forward bias condition, when a positive voltage was applied to the metal plate, the top of the conduction band bent downward and was closed to the Fermi level.

In the I-t measurement, the transient switching time of the $Bi_4Mn_{0.4}Ti_{2.6}O_{12}$ / n-Si thin film device was faster than that of the $Bi_4Mn_{0.3}Ti_{2.7}O_{12}$ / n-Si thin film device and also faster and faster with increasing Mn composition. This meant that internal energy was aligned in the same direction as the applied electric field. Thus the present research allowed more economical coating, technical simplicity and easy adaptability. Moreover, the film fabricated with sol-based method were quite promising candidate for memory device applications.

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