Structural and electrical properties of ferroelectric BiFeO₃/HfO₂ gate stack for nonvolatile memory applications

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Difficulties in the fabrication of direct interface of ferroelectric BiFeO₃ on the gate of ferroelectric field effect transistor (FeFET) is well known. This paper reports the optimization and fabrication of ferroelectric/dielectric (BiFeO₃/HfO₂) gate stack for the FeFET applications. RF magnetron sputtering has been used for the deposition of BiFeO₃, HfO₂ films and their stack. X-Ray diffraction (XRD) analysis of BiFeO₃ shows the dominant perovskite phase of (104), (110) orientation at $2\theta = 32^\circ$ at the annealing temperature of 500°C. XRD analysis also confirms the amorphous nature of the HfO₂ film at annealing temperature of 400°C, 500°C and 600°C. Multiple angle analysis shows the variation in the refractive index between 2.98–3.0214 for BiFeO₃ and 2.74–2.9 for the HfO₂ film with the annealing temperature. Metal/Ferroelectric/Silicon (MFS), Metal/Ferroelectric/Metal (MFM), Metal/Insulator/Silicon (MIS), and Metal/Ferroelectric/Insulator/Silicon (MFIS) structures have been fabricated to obtain the electric characteristic of the ferroelectric, dielectric and their stacks. Electrical characteristics of the MFIS structure show the memory improvement from 2.7 V for MFS structure to 4.65 V for MFIS structure with 8 nm of buffer dielectric layer. This structure also shows the breakdown voltage of 40 V with data retention capacity greater than 9×10^9 iteration cycles.

Keywords: Endurance; ferroelectric; high-*k* dielectric; memory window; MFIS.

1. Introduction

Ferroelectric films have shown its potential in many applications such as transducers,^{1–4} detectors,^{5–7} optical devices,^{8–10} dynamic random access memories (DRAMs)^{11–13} and ferroelectric memories.^{14–16} In the last few decades, properties of ferroelectric materials have been widely explored for the memory applications. Ferroelectric materials show spontaneous polarization that can be reversed under the influence of external electric field.^{17,18} Ferroelectric materials have noncentrosymmetric structure,^{18,19} which can be realized by the crystals of double-well potential, where at least one set of ion shows the stable structure by sitting on the same side of the double well giving rise to the region called domain.^{20,21} The ions in the domain sit on the same side of the double wells giving rise to the net dipole moment per unit volume, known as polarization. Net polarization is used to realize two stable states in the memory capacitor that defines the bit “1” or “0”.^{22,23}

Ferroelectric random access memories (FeRAMs) with 1T-1C architecture have been commercially fabricated by different industries which offer the nonvolatile data storage capacity with high reliability and faster read/write speed than

the currently existing FLASH memory,^{24–28} but also faces several challenges such as destructive readout and higher cost.^{24,29,30}

It is the reason that FeRAM is still not preferred for the large data storage. To simplify the destructive readout and higher cost issue, ferroelectric field effect transistor (FeFET) with direct integration of ferroelectric layer on the MOSFET was proposed.^{22,31} The FeFET structure solves the problem of 1T-1C structure but suffers from ferroelectric–silicon reaction and interdiffusion due to the thermal instability of ferroelectric layer on direct integration with silicon. It is the reason why no FeFET-based FeRAM was commercially fabricated. Further, to solve the issue of ferroelectric and silicon incompatibility, it was proposed that an insulator layer should be introduced between the ferroelectric and silicon resulting into the metal/ferroelectric/insulator/silicon (MFIS) stack at the gate of the MOSFET.³² Insulator layer ultimately improves the interface between the silicon and ferroelectric, prevents the Fe–Si reaction and interdiffusion, and charge injection from the silicon to ferroelectric layer.³³

In the present work, BiFeO₃ as the ferroelectric and HfO₂ as the insulator layer deposited by the RF sputtering have

been selected for the MFIS gate stack fabrication. BiFeO₃ as a lead-free multiferroic material having high remnant polarization.^{34–38} and HfO₂ due to its high bandgap (25) and good thermal stability with silicon³⁹ has been selected in this work.

2. Experimental Procedure

Silicon substrate *p*-type, (100) orientation having resistivity 1–5 Ω-cm has been used for the thin film deposition and capacitor fabrications. The substrates have been cleaned using standard Radio Corporation of America (RCA) cleaning procedures prior to the loading of wafers into the vacuum chamber. RF magnetron sputtering operated at the frequency of 13.56 MHz has been used for the thin film deposition of BiFeO₃ (200 nm) and HfO₂. The system has been pumped down to 5×10^{-6} mbar and the deposition was carried out at 9×10^{-3} mbar chamber pressure. Deposited film annealing has been carried out in a quartz tube furnace in the presence of nitrogen for different temperature range. Top platinum and aluminum metal contacts have been fabricated through a shadow mask of circular opening 3.14×10^{-4} cm² using sputtering and thermal evaporation processes, respectively. For the Metal/Ferroelectric/Metal (MFM) structure, 100 nm top and bottom platinum electrode has been fabricated by DC sputtering at the power of 100 W. X-Ray diffraction (XRD) analysis for the crystal orientation detection and multiple angle ellipsometric analysis for the film thickness, refractive index and absorption constant detection has been used.

Metal/Ferroelectric/Silicon (MFS), MFM, Metal/Insulator/Silicon (MIS), and Metal/Ferroelectric/Insulator/Silicon (MFIS) structures have been fabricated and electrically characterized to obtain the capacitance, leakage current density, remnant charges, coercive electric field, breakdown voltage and endurance using Keithley 4200 Semiconductor characterization system.

3. Results and Discussion

Figures 1(a) and 1(b) show the XRD pattern of the BiFeO₃ and HfO₂ film annealed at different temperature, respectively.

BiFeO₃ film annealed at 500°C shows the maximum intensity peak at $2\theta = 32^\circ$ indicating the (104), (110) orientation and perovskite phase at the annealing temperature of 500°C. Several secondary intensity peaks have been observed at the annealing temperatures of 400°C and 600°C, which show the existence of different phases possible due to the noncrystallized deposited film at 400°C and due to the loss of film stoichiometry at 600°C. Amorphous HfO₂ film structure has been evident from the XRD pattern, where no significant intensity has been observed. Ellipsometric analysis has been carried out to obtain the refractive index at different annealing temperature and the results obtained are shown in Fig. 2.

Maximum refractive indices of 3.03 and 2.9 have been observed for the BiFeO₃ and HfO₂ film at the annealing temperature of 500°C. Higher refractive index indicates the

Fig. 1. XRD pattern of (a) BiFeO₃, and (b) HfO₂ film annealed at 400°C, 500°C and 600°C.

Fig. 2. Refractive index of BiFeO₃ and HfO₂ film annealed at 400°C, 500°C and 600°C.

increased film density,^{40,41} possibly due to the film crystallization, as evident from the XRD data in case of the BiFeO₃ film. After the structural characterization, MFS structure has been fabricated and electrically characterized to obtain the C-V and J-V parameters shown in Fig. 3.

Maximum memory window of 2.7 V has been observed for the MFS structure with ferroelectric film annealed at 500°C. Maximum memory window at 500°C is due to the crystallized film even evident from the XRD and ellipsometric analysis. The memory window improved from 1.5 V to 2.7 V with the annealing temperature from 400°C to 500°C and further reduced to 2.3 V as the annealing temperature increased to 600°C. The leakage current density of the orders 10⁻⁵ A/cm² and 10⁻⁶ A/cm² has been observed for films annealed at different temperature at the voltage bias of -10 V and +10 V, respectively. As the ferroelectric film annealed at 500°C shows crystalline perovskite phase and maximum memory window, we have fabricated the MFM structure to

(a)

(b)

(c)

Fig. 3. (a) C-V, (b) memory window versus annealing temperature, and (c) J-V characteristics of the MFS structures annealed at 400°C, 500°C and 600°C.

Fig. 4. (a) Sample input voltage and current, (b) charge versus voltage hysteresis loop for the MFM structure with ferroelectric film annealed at 500°C.

obtain the hysteresis characteristic with ferroelectric film annealed at 500°C, as shown in Fig. 4.

The MFM structure shows the proper hysteresis loop with remanent charge $7.07 \times 10^{-5} \mu\text{C}$ and coercive voltage of -2.4 V for the input voltage sweep of $\pm 5 \text{ V}$. After the electrical characterization of ferroelectric film, the electric properties of dielectric film have been investigated by obtaining the $C-V$ and $J-V$ characteristics of the MIS structure, as shown in Fig. 5.

Electrical characteristics show the proper interface of HfO_2 film with silicon with low interface defect density as observed from the $C-V$ characteristics. Leakage current density of the orders 10^{-1} A/cm^2 and 10^{-6} A/cm^2 has been observed for the gate voltage of -10 V and $+10 \text{ V}$,

respectively. Higher leakage current density at the negative gate bias is due to the charge injection from the silicon to the insulator layer.

After ferroelectric and insulator film optimization and electrical characterization, the MFIS gate stack has been fabricated with insulator layer of thicknesses 3, 8 and 13 nm. The MFIS structures were electrically characterized to obtain the capacitance versus voltage characteristics, as shown in Fig. 6.

Maximum memory window of 4.65 V has been observed for the insulator layer of 8 nm thickness at the voltage sweep of $\pm 15 \text{ V}$. Lower memory window of 1.7 V and 3.1 V has been observed for the insulator layer thicknesses of 3 nm and 13 nm, respectively. For 3 nm buffer layer, lower memory

Fig. 5. (a) $C-V$ and (b) $J-V$ characteristics of the MIS structure with insulator film annealed at 400°C, 500°C and 600°C.

Fig. 6. (a) C-V, and (b) memory window characteristic for different insulator layer thickness.

window is possible due to the diffusion of BiFeO₃ through the buffer layer to the silicon substrate providing the direct contact path for the charges to flow, hence increased leakage and reduced memory window. Buffer layer of lower thickness does not provide sufficient shielding to the ferroelectric film to diffuse through it and reach to the silicon substrate. Also, the charges at high electric field tunnel through the buffer layer of low thickness resulting in the increased leakage current, hence low memory window and data retention characteristics. For 13 nm buffer layer, the buffer layer thickness is increased which improves the charge leakage and ferroelectric diffusion to silicon but have the disadvantage of higher voltage drop across it. Due to higher voltage drop, the net voltage available to the ferroelectric layer decreased

hence lower polarization and lower memory window. The 8 nm buffer layer thickness provides the sufficient potential barrier to the charge tunneling from ferroelectric to silicon (less than 13 nm HfO₂ film) along with the ferroelectric diffusion to silicon. At the same time, the voltage drop across the buffer layer is low as compared to the 13 nm HfO₂ film. These are the reasons which improve the memory window of the MFIS structure with 8 nm buffer layer as compared to the 3 nm and 13 nm buffer layers. Now, the MFIS structure with 8 nm buffer layer has been characterized to investigate the retention time and the result obtained is shown in Fig. 7.

Results clearly indicate that the MFIS structure shows no decrease in the positive and negative polarizations for the iteration cycles up to 9×10^9 . The breakdown characteristic

Fig. 7. Data retention characteristic of the MFIS structure with 8 nm buffer layer annealed at 500°C.

Fig. 8. Breakdown voltage of MFS and MFI_{8nm}S structure with ferroelectric and dielectric films annealed at 500°C.

of the same structure and the MFS structure annealed at 500°C has been investigated and the result obtained is shown in Fig. 8.

With the introduction of the 8 nm buffer layer, the breakdown voltage of the MFIS structure improved to 41 V from 35 V of the MFS structure. Improved breakdown voltage is due to the increased stack thickness and the strength provided by the HfO₂ layer along with ferroelectric layer.

4. Conclusion

In conclusion, perovskite BiFeO₃ film has been prepared at the annealing temperature of 500°C. Effect of buffer layer sandwiched between ferroelectric and silicon substrate improves the memory window, breakdown and data retention capacity. The fabricated structure can be used as a potential candidate for the FeFET nonvolatile memory application.

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