Electrodeless Characterization of Memorized States of MFIS Structure by Photoreflectance Spectroscopy

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SrBi$_2$Ta$_2$O$_9$ (SBT)/SiO$_2$/Si structures have been characterized by photoreflectance spectroscopy (PRS) without electrode formation. SBT film was deposited on SiO$_2$/n-Si by the metal-organic decomposition (MOD) method and annealed in O$_2$ atmosphere at 600°C. The voltage was applied by attaching ITO transparent electrode during PRS measurement. The PRS spectral intensity of SBT/SiO$_2$/Si structure has hysteresis characteristics as well as C-V curve. Additionally, the spectral intensity gradually decreases with time similar with reduction of the capacitance. These results means that the spectral intensity gives the ferroelectricity of SBT film in SBT/SiO$_2$/Si structure so that it is considered that characterization of MFIS structure without electrode can be measured by PRS.

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I. INTRODUCTION

Recently, ferroelectric random access memory (FeRAM) has attracted much attention as it is non-volatile, high-speed and low-loss memory. In particular, metal-ferroelectric-insulator-semiconductor (MFIS) FET has been expected as one transistor (1-T) type memory because of its nondestructive read-out and scalability[1]. However, the retention time of MFIS-FET memory becomes degraded according to some factors such as leakage current and the relaxation of ferroelectric polarization[2]. Therefore, characterization of memorized states in MFIS structure is very important.

Photoreflectance spectroscopy (PRS), which is one of modulated reflectance spectroscopy techniques[3], gives stress and surface potential of semiconductor without electrode. PRS spectrum can be easily analyzed by the third differential form of the reflectance[3, 4]. It can be applied to in-situ or in-line monitoring due to these features. It was manifested that PRS spectrum reflects the remnant polarization or the stress by piezoelectric effect of MFIS structure in our previous works[5, 6]. However, previous measurement method has weak points such as noisy spectrum since Au semi-transparent film which absorbs the probe light is used for electrode.

Consequently, in this work, we have applied voltage to FIS structure by firmly attaching a plate glass with indium tin oxide (ITO) transparent electrode during PRS measurement. Moreover, it is considered that this method allows quick and damage-free characterization of memorized states of MFIS structure without electrode formation.

II. THEORY

When the Si surface is irradiated with the modulation light, photo-carrier generation occurs, and gives surface potential of Si inappreciable change. Dielectric function is modulated by this perturbation of the surface field, and this change is sharply reflected to optical property around band edge. The PRS spectrum, which is ratio of reflectance variation by laser irradiation to reflectance ($\Delta R/R$) is expressed by a following equation as a function of photon energy $E$[3],

$$\frac{\Delta R}{R}(E) = \Re \left\{ Ae^{i\theta} \left( E - E_{CP} + i\Gamma \right)^{-n} \right\},$$

(1)

where $A$ and $\theta$ are the intensity and the phase factors of the spectrum, respectively, $E_{CP}$ is the critical point energy of Si energy band structure, $\Gamma$ is the broadening factor of the spectrum, and the $n$ value is number dependent on dimensionality of band edge, such as 3 for the $E_1(\Lambda_2-\Lambda_1)$ critical point. The PRS spectral intensity is proportional to Si surface potential $\Psi_s[7]$, 

$$|A| \propto \ln \left( B \exp \left( \frac{\Psi_s}{kT} \right) + 1 \right),$$

(2)

where $B$ is a constant. The calculated capacitance-voltage ($C-V$) curve[8] and PRS spectral intensity of SBT(dielectric constant $\varepsilon = 180$)/SiO$_2$($\varepsilon = 3.9$)/n-Si

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structure are shown in Fig. 1. The spectral intensity is normalized to equal 1 at −1 V. It is found that the PRS spectral intensity increases with increasing negative voltage.

III. EXPERIMENTAL

After RCA cleaning and removing native oxide, n-type Si (100) wafers (ρ ~ 0.02 Ω cm) were oxidized in O₂ atmosphere at 700°C. Then SBT films (200–500 nm) were deposited by the metal-organic decomposition (MOD) method and post-annealed in O₂ atmosphere at 600°C for 10–30 min.

The samples were characterized by PRS and C-V measurement. For PRS measurement, the reflectance and its small reflectance change modulated by laser irradiation (Ar⁺ laser, wavelength 488 nm, power 0.2–1.0 W) were measured in the spectral range from 3.2 to 3.7 eV. All PRS measurements were carried out at room temperature (~ 300 K) in the air. The voltage was applied by firmly attaching a plate glass with ITO transparent electrode during PRS measurement. For C-V measurement, Au top electrode and AuSb bottom electrode were deposited by vacuum evaporation.

IV. RESULTS AND DISCUSSION

Figure 2 shows the C-V curve of Au/SBT/SiO₂/n-Si. The curve shows a counterclockwise hysteresis loop so that it is found that deposited SBT film has the ferroelectricity. However, the C-V characteristic behavior in Fig. 2 is smaller than the calculated one in Fig. 1. C-V curve in Fig. 1 is calculated as the dielectric constant of SBT is 180, but it is considered that deposited SBT film has smaller value of the dielectric constant. The dielectric constant estimated from the maximum capacitance (1.32 F/cm²) of C-V curve in Fig. 2 is about 7, which is too small value. It suggests that there are an interfacial layer between SBT and SiO₂ or SiO₂ and Si substrate grown by the mutual diffusion of constituent atoms in each layer, which has smaller dielectric constant than SBT film. Figure 3 shows applied voltage dependence of PRS spectral intensity. The spectral intensity increases with increasing negative voltage. PRS spectral intensity is expressed as a function of Si surface potential as shown in Eq. (2) which increases by application of negative voltage.

Moreover, PRS spectral intensity has hysteresis characteristics which the intensity of sweeping direction from negative to positive (open square) is larger than one of inverse direction (open triangle) between 0 V and +2 V. This result means that Si surface potential differs according to the sweeping direction because of the polarization in SBT film. The dashed line shows the spectral intensity calculated from C-V curve shown in Fig. 2. The maximum value of the calculated intensity is fitted that of the measured intensity. The hysteresis direction of PRS spectral intensity agrees with calculated one, but the hysteresis width is broader. It must be noted that measure-
ment conditions of PRS are different from that of $C-V$ measurement, such as measurement frequency, with or without a light irradiation, the shape of electrode and so on. Therefore, although the PRS spectral intensity correlates $C-V$ curve, they are not necessarily correspondent each other. Thus, it is difficult to quantitatively obtain the capacitance value from PRS spectral intensity, if not impossible. However, it is considered that PRS can provide an qualitative indication of the performance of MFIS structures.

The time dependence of PRS spectrum of SBT/SiO$_2$/Si structure after writing $-5$ V and hold at 0 V is shown in Fig. 4. The spectral intensity gradually decrease after writing process. Figure 5 shows the time dependence of difference of retained capacitances of SBT/SiO$_2$/Si written at $+5$ V and $-5$ V (open square), and the time dependence of PRS spectral intensity (close circle). It is found that these time dependencies show the same tendencies. Si surface potential decreases with decreasing of charge injection or the remanent polarization in SBT film. Therefore, it is considered that PRS spectral intensity in Fig. 5 reflects retention property of SBT film so that retention property of MFIS structure can be characterized by measurement of PRS spectral intensity.

**V. SUMMARY**

The memorized states of SBT/SiO$_2$/Si structure have been characterized by PRS with applying voltage by attaching ITO glass instead of forming electrode. The PRS spectral intensity of SBT/SiO$_2$/Si has hysteresis characteristics to applied voltage as well as the $C-V$ curve. It is considered that PRS spectral intensity reflects hysteresis characteristics of SBT/SiO$_2$/Si structure. The PRS spectral intensity gradually decrease after writing process. This result means that Si surface potential decreases with decreasing of charge injection or the remanent polarization in SBT film. From these results, it is considered that PRS can be applied to characterization of SBT ferroelectricity in MFIS structure without electrode.

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