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Author(s)	堀井, 貞義
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Description	Supervisor:堀田 将, 材料科学研究科, 博士

Fabrication of Memory Structure with Epitaxial Ferroelectric Thin Film

School of Material Science Sadayoshi Horii

FeRAM (Ferroelectrics RAM) is non-volatile memory to use remanent polarization of ferroelectric materials and has high potential to replace DRAM and flush-memories. Although it has been investigated for more than 25 years, the integration of FeRAM is from 256k to 1M and is behind the present DRAM in several generations. One of the reasons is unstability of the ferroelectric properties because the used ferroelectric thin films are polycrystalline. On the other hand, a single crystalline thin film has (1) the stable property, (2) the large remanent polarization and (3) ideal isotropic property to investigate easily the mechanism of fatigue and retention phenomena, compared to polycrystalline film. Then, in order to apply the epitaxial ferroelectric thin film to the 256M bit FeRAM with STC (Stacked Cell) structure, the goal of this study is to fabricate an epitaxial ferroelectric thin film (1) whose polarization is saturated at a low voltage such as 1.5 V, (2) which has a large remanent polarization more than 120 $\mu C/cm^2$ and (3) which is fatigue-free for more than switching cycles of 10^{10} times, and to investigate the properties of the epitaxial ferroelectric thin film. The suitable materials for the STC structure were investigated and the structure was decided to be IrO_2/PZT ($PbZr_xTi_{1-x}O_3$)/Ir/ZrN/Si. It is included in the goal of this study that the contact resistivity between the ZrN thin film and the Si substrate should be less than $0.1\mu\Omega cm^2$ in order to apply this structure to 256M bit FeRAM.

At first, in order to demonstrate the superior property of the epitaxial film, the epitaxial (001)PZT film on epitaxial (100)Ir/(100)YSZ ($(ZrO_2)_{1-x}(Y_2O_3)_x$)/(100)Si structure without the problem of contact resistance was fabricated and investigated. The epitaxial (001) 30~280 nm-thick PZT films on epitaxial (100)Ir/(100)YSZ /(100)Si structure showed the well-saturated hysteresys loops with good squareness between the polarization and voltage. Also, by removing the surface decomposed layer of the PZT film with HNO_3 solution treatment prior to deposition of IrO_2 top electrodes, the formation of degraded layer between the IrO_2 top electrode and the PZT film was suppressed even after IrO_2 deposition. So, the remanent polarization and the leakage current of the treated PZT film increased and decreased, respectively, and the fatigue property of the PZT film was improved. Also, it was shown that the film thickness dependence of the PZT film and the fatigue property can be explained by the model of carriers injection into the degraded layer at the interface between the PZT film and the electrode. As a typical result, the polarization of 100 nm-thick PZT/Ir/YSZ/Si film was saturated at 1.5 V and its PZT film had the remanent polarization 2Pr of $75\mu C/cm^2$. Therefore, it can be applied to 128M bit FeRAM.

Next, we investigated the epitaxial PZT/Ir/ZrN/Si structure. The ZrN film deposited at 600 ºC on an Si substrate was grown hetero-epitaxially with cube-on-cube relationship. However, it was found that the Ir film deposited on the ZrN film was polycrystalline because the surface of the ZrN film was easily oxidized in the air before the Ir film deposition. To solve this problem, the surface oxidized ZrN layer was removed somewhat and the re-oxidation was suppressed by treating with HF and hydrazine solution, which was confirmed by RHEED observation and the XPS measurement. Moreover, it was found that the ZrN film was oxidized by residual oxygen components activated by Ir catalysis in the deposition chamber. We solved this problem to use a Ir+Zr composite target in which the Zr pellets were circularly placed on the Ir metallic target. Since the residual oxygen compounds were reduced by gettering effect of the sputtered Zr atoms, the oxidation of the ZrN film was perfectly suppressed during the Ir film deposition. However, the Ir film deposited on the HF+hydrazine treated epitaxial (100)ZrN film was (100) and (110) oriented epitaxial film probably not only because the ZrN film was poor crystalline quality and but also because the surface roughness was increased after HF+hydrazine treatment. Although the 200 nm-thick PZT film deposited on the Ir/ZrN/Si structure was also a (001) and (101) oriented epitaxial film, the ferroelectric property of the PZT film was almost the same as an epitaxial 150 nm-(001)PZT film on the Ir/YSZ/Si structure. From these results, it can be concluded that if an epitaxial (100) oriented Ir film with high crystalline quality were obtained by improving the crystalline quality of the epitaxial (100)ZrN film, an epitaxial STC structure could be adapted at least for 128 M bit FeRAM.