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Substrate Orientation Dependence of the Properties of Metal-Ferroelectric $BaMgF_4$-Silicon Capacitors by Post-Deposition Annealing

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A substrate orientation dependence of metal-ferroelectric $BaMgF_4$-silicon capacitors by a rapid thermal annealing was investigated. The fluoride films were deposited on Si(100), (110) and (111) oriented wafers in an ultra-high vacuum system at substrates temperature of 300 °C. A post-deposition annealing was conducted for 10 seconds at 600 °C. The results were found out to increase the resistivity of the ferroelectric $BaMgF_4$ film from a typical value of $1\sim2\times10^{11}$ Ω·cm before the annealing to about 5×10^{13} Ω·cm at 1 MV/cm and reduce the interface state density of the $BaMgF_4$/Si interface to $5\sim8\times10^{10}$ /cm^2·eV. The typical remanent polarizations of the $BaMgF_4$ films on the (100) and (111) oriented silicon wafers were 0.5~0.6 μC/cm^2 and that of the films on the (110) wafer was 1.2 μC/cm^2.

1. Introduction

Metal-ferroelectric-semiconductor FETs(MFSFETs) are key devices for memory devices[1] such as ferroelectric memory FETs(FEMFETs) and for functional neuron devices[2]. The materials requirements for the ferroelectric film in such device structures necessitate deposition directly onto the semiconductors. In these cases, it is necessary that the film maintains its ferroelectric properties on the semiconductor and the interface state density at the ferroelectric film/semiconductor interface must be small for normal FET operation. So far, most ferroelectric materials widely studied are oxides such as $Bi_4Ti_3O_{12}$, $BaTiO_3$, $PbTiO_3$, and PZT. Thin films of these materials usually exhibit good ferroelectric properties itself on a metal electrode such as the platinum. It is difficult, however, to preserve ferroelectricity on semiconductors due to reaction between the oxides and semiconductor surface. So, there are few reports of good MFS devices. Recently, non-oxide ferroelectric fluoride $BaMgF_4$ films grown by molecular beam epitaxy(MBE) on semiconductor structures have been reported. Such structures may expected to exhibit good interface properties due to the fabrication of the fluoride film in an ultra-high vacuum(UHV) system. However, ferroelectric fluoride films on Si are not so good electrically due to their low resistivity, low dielectric breakdown field and time dependent deterioration of several properties. More recently, such problems have been partially improved[3] by post-deposition annealing.

This paper describes the properties of metal-ferroelectric $BaMgF_4$-silicon capacitors by post-deposition rapid thermal annealing(RTA) and investigates an effects of the substrate orientation dependence.

2. Experimental

$BaMgF_4$ films were deposited in a ultra high vacuum(UHV) system. Boron doped p-type silicon (100), (110) and (111) oriented wafers with resistivities of approximately 1~10 Ω·cm were used. $BaMgF_4$ films were deposited by evaporating BaF_2(99.999% pure) and MgF_2(99.999% pure) grains, mixed in equimolecular portions in a carbon crucible. Fluoride films ranging from 100 to 160 nm thick were deposited at a temperature of 300 °C with a deposition rate of 0.1~0.2 nm/s. After deposition of the $BaMgF_4$ film, the RTA was done for 10 seconds at 600 °C in a vacuum of 0.1 Torr, using a home-made RTA apparatus. The films were analyzed structurally by X-ray diffraction(XRD). The hysteresis measurements were performed using a RT-66A(Radiant Technologies, Albuquerque, NM) test system. Current-Voltage(I-V) measurements were performed using a HP model 4145B semiconductor parameter analyzer. The capacitance-voltage(C-V) curves were measured with a 1 MHz C-V plotter using deposited Al electrode dot patterns with 200 μm diameter on the films.

3. Results and Discussion

Figure 1 shows I-V characteristics denoted by current density and electric field of MFS capacitors biased at accumulation state(that is, negative bias voltages). In the figure, the dashed curve was the characteristic of the as-deposited sample and the solid curve was for the rapidly thermal annealed sample. The breakdown field of the $BaMgF_4$ film was increased from a typical value of $1\sim2\times10^5$ V/cm before the RTA to more than 1×10^6 V/cm at a current density of 1 μA/cm^2. The resistivity was increased from a value of $1\sim2 \times 10^{11}$ Ω·cm before to more than 5×10^{13} Ω·cm at that breakdown field. The increases of the breakdown field and resistivity may be explained by improvement of the crystalline quality or densification of the film during annealing. In fact, it was observed that the refractive index of the film at a wavelength of 632.8 nm was increased by the annealing, typically from 1.45 to 1.49 and the film thickness was reduced by about 4 %.

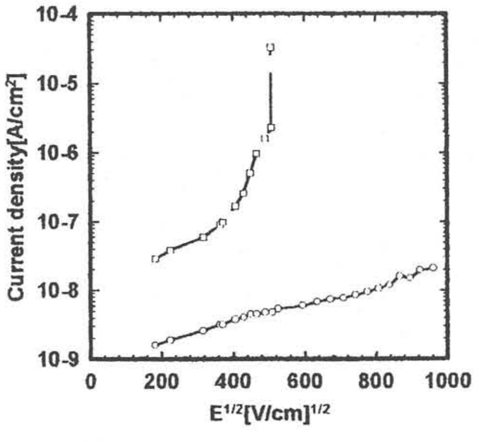

Fig. 1. I-V characteristics denoted by current density and square root of electric field of MFS capacitors biased at accumulation state.

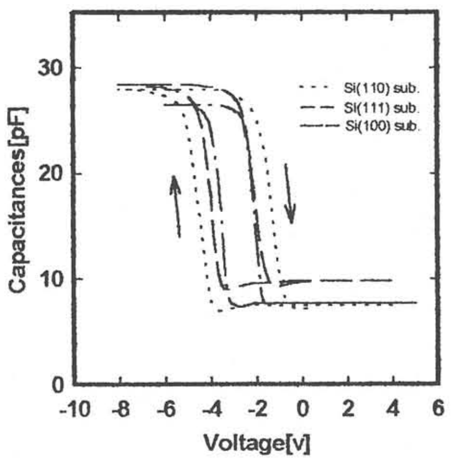

Fig. 2. 1 MHz C-V characteristics of MFS capacitors fabricated on Si(100), (110) and (111) oriented substrates, respectively.

Figure 2 show 1 MHz C-V characteristics of MFS capacitors fabricated on Si(100), (110) and (111) oriented substrates, respectively, under incandescent lamp illumination. The reason for illumination during testing is to obtain certain C-V curves varies from accumulation to inversion states. All of the C-V curves show that the capacitance values varies from the accumulation to inversion states and also hystereses and the direction of hystereses are consistent with ferroelectric polarization switching, rather than charge injection. Notice the hysteresis window of each curve due to ferroelectric hysteresis is different according to the substrate orientation. The memory window of the film on the (110) wafer was largest. In Fig. 2, our typical samples showed that the C-V curves were shifted in a negative direction(that is, negative threshold voltage). This might be due to charges existing in the $BaMgF_4$ film and at $BaMgF_4$/Si interface. The dielectric constant calculated from accumulation region shown in Fig. 2 was about 13, which was close to the reported value[4)] for the b axis(14.75 at 10 MHz) of $BaMgF_4$. This agreement might be related to the crystallinity of our annealed film which will be showing a polycrystalline nature with preferred b-axis orientation. The minimum interface state density around the midgap derived from the C-V curve of Fig. 2 was ranged from 5 to 8 $\times 10^{10}$ /cm^2·eV.

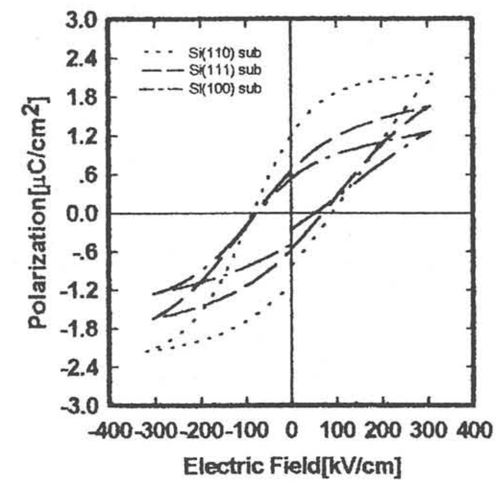

Fig. 3. Polarization hysteresis loop of MFS capacitors fabricated on Si(100), (110) and (111) oriented substrates.

Figure 3 show Sawyer-Tower results of MFS capacitors fabricated on Si(100), (110) and (111) oriented substrates under incandescent lamp illumination measured using a RT-66A test system. The typical remanent polarizations(P_r) of the $BaMgF_4$ films on the (100) and (111) oriented silicon wafers were 0.5~0.6 μC/cm^2 and that of the films on the

(110) wafer was 1.2 $\mu C/cm^2$. The typical coercive fields(E_C) for each sample ranged from 60 kV/cm to 100 kV/cm. This difference might be related to the orientation states of the $BaMgF_4$ films on each silicon wafer.

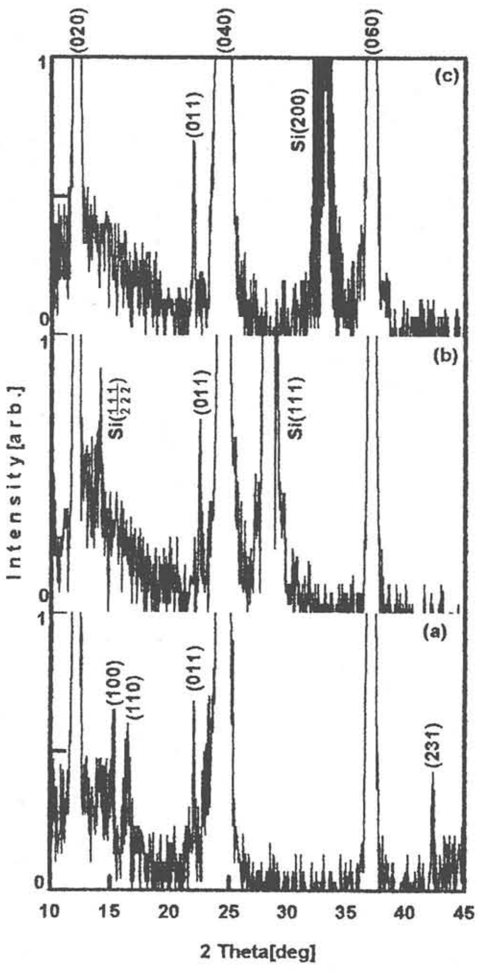

Fig. 4. XRD patterns of the $BaMgF_4$ films on (a) Si(110), (b) Si(111) and (c) Si(100) oriented substrates.

Figure 4(a), 4(b) and 4(c) show XRD patterns of the $BaMgF_4$ films on Si(110), (111) and (100) oriented substrates, respectively. In addition to the all XRD patterns showed polycrystalline natures with preferred b-axis orientation, some different weak peaks appeared in the $BaMgF_4$ film on Si(110) oriented substrate, including three representing the (100), (110) and (231) orientation. It is considered that these peaks might be related to the enlargement of the hysteresis memory window and the remanent polarization of the $BaMgF_4$ film, because that peaks included polycrystalline natures with a-axis orientation.

4. Conclusion

Properties of metal-ferroelectric $BaMgF_4$-silicon capacitors depend on substrate orientation by a rapid thermal annealing was investigated. The breakdown field of the $BaMgF_4$ film was increased from a typical value of 1~2 $\times 10^5$ V/cm before the RTA to more than 1×10^6 V/cm at a current density of 1 $\mu A/cm^2$. The resistivity of the RTA treated ferroelectric $BaMgF_4$ film was about 5×10^{13} Ω·cm at 1 MV/cm. The interface state density of interface of the $BaMgF_4$ on each orientation of Si was 5~8$\times 10^{10}$ /cm^2·eV. The typical remanent polarizations of the $BaMgF_4$ films on the (100) and (111) oriented silicon wafers were 0.5~0.6 $\mu C/cm^2$ and that of the films on the (110) wafer was 1.2 $\mu C/cm^2$. The enlargement of the hysteresis memory window and the remanent polarization of the $BaMgF_4$ film on Si(110) might be related to peaks included polycrystalline natures with a-axis orientation.

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References

1) S.-Y. Wu, IEEE Trans. Electron Devices, **ED-21** (1974) 499.
2) H. Ishiwara, Jpn. J. Appl. Phys., **32** (1993) 442.
3) K. -H. Kim, J. -D. Kim and H. Ishiwara, Appl. Phys. Lett., **66** (1995) issue of the 5 June 1995.
4) S. Sinharoy, H. Buhay, M. G. Burke, D. R. Lampe, and T. M. Pollak, IEEE Trans. Ultrason. Ferroelectr. Freq. Contr., **38** (1991) 663.