Journal of Korean Institute of surface Engineering
Vol. 29, No. 6, Dec., 1996

CHARACTERISTICS OF HETEROEPITAXIALLY GROWN Y_2O_3 FILMS BY r-ICB FOR VLSI

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ABSTRACT

Y_2O_3-based metal-insulator-semiconductor (MIS) structure on p-Si(100) has been studied. Films were prepared by UHV reactive ionized cluster beam deposition (r-ICBD) system. The base pressure of the system was about 1×10^{-9} Torr and the process pressure 2×10^{-5} Torr in oxygen ambience. Glancing X-ray diffraction(GXRD) and in-situ reflection high energy electron diffracton(RHEED) analyses were performed to investigate the crystallinity of the films. The results show phase change from amorphous state to crystalline one with increasingqr acceleration voltage and substrate temperature. It is also found that the phase transformation from $Y_2O_3(111)//Si(100)$ to $Y_2O_3(110)//Si(100)$ in growing directions takes place between 500℃ and 700℃. Especially as acceleration voltage is increased, preferentially oriented crystallinity was increased. Finally under the condition of above substrate temperature 700℃ and acceleration voltage 5kV, the Y_2O_3 films are found to be grown epitaxially in direction of $Y_2O_3(110)//Si(100)$ by observation of transmission electron microscope(TEM). Capacitance-voltage and current-voltage measurements were conducted to characterize Al/Y_2O_3/Si MIS structure with varying acceleration voltage and substrate temperature. Deposited Y_2O_3 films of thickness of nearly 300Å show that the breakdown field increases to 7~8MV/cm at the same conditon of epitaxial growing. These results also coincide with XPS spectra which indicate better stoichiometric characteristic in the condition of better crystalline one. After oxidation the breakdown field increases to 13MV/cm because the MIS structure contains interface silicon oxide of about 30Å. In this case the dielectric constant of only Y_2O_3 layer is found to be ϵ15.6. These results have demonstrated the potential of using yttrium oxide for future VLSI/ULSI gate insulator applications.

INTRODUCTION

It is well known, not to mention, that the microelectronics(ME) technology has greatly affected present and future industry. The growing velocity of ME technology which has been led by semiconductor is rapidly increasing with the expansion of information industry. In the technology of semiconductor device, in order to accomplish the high device integration, thin film growing technique should be developed to get the films that have

characteristics of high dielectric constant and high breakdown field strength.

The most popular insulating thin film, SiO_2 has excellent properties to be used in insulator, but it must be thinner in its thickness to be used in MOS gate insulator for ULSI and VLSI. The thin film of SiO_2($<7\sim8$nm) always has high pin hole density resulting in inducing the tunneling current conduction. Therefore, the film has low breakdown field strength and high leakage current.[1] It is difficult for the thin film of SiO_2 to be used in insulator for ULSI. To use the high dielectric material as a gate insulator for ULSI, it is needed that the films have not only high dielectric constant but also high breakdown field strength. From this point of view, Y_2O_3, ZrO_3, CaF_2 and CeO_2 have lively studied. The most important factor for epitaxial growing is lattice match with substrate. The lattice misfit factors with Si of ZrO_2, CaF_3 Y_2O_3 are 3.3%, 0.6%, 2.4%, respectively, while the factor of CeO_2 is very low 0.35%. CeO_2 is very suitable to grow epilayer on Si and use the stroage capacitor in DRAM.[2] Y_2O_3 has just a little larger lattice mismatch factor than CeO_2 but draws very attractive attention. Because yttrium more easily can be bonded with oxygen than Ce and Y_2O_3, relatively more easily form the epitaxial layer on Si than others with larger lattice match factor.[3,11]

In this study, to grow excellent film-quality, reactive ionized cluster beam(r-ICB) deposition technique was employed. In many cases using the ICB, it was reported that ICB showed high quality thin film formation in film density, adhesion, smoothness, and crystallinity.[12-14] In present paper, MIS structure with Y_2O_3, films by r-ICB deposition was studied. The crystallinity and the stoichiometry were investigated under the various process conditions. The electrical characteristics such as I-V and C-V were also examined.

EXPERIMENTAL PROCEDURE

It is impossible to evaporate the stable Y_2O_3 directly due to its high melting temperature, 2410℃. In this study, Y_2O_3 films were fabricated by reactive ICBD method including the O_2 gas as a reactive gas and the yttrium cluster as an ion cluster beam. To obtain the ultra high vacuum, LN_2 cold trap was installed in the chamber to remove the impurity in deposition process. The loaded Si(100) wafer was heated up to 1000℃ by e-beam bombordment to completely remove the native oxide on Si, and the clean Si surface was examined by RHEED.

The base pressure of the growth chamber was maintained below 1×10^{-9} Torr. During the deposition, the process pressure was fixed at 2×10^{-5} Torr in oxygen ambience. The electron gun bias(Ve) and electron beam current(Ie) to ionize the yttrium cluster were fixed at 400V and 100mA, respectively, and the deposition rate was controlled at the rates range from 0.4 to 0.5 Å/sec.

In order to examine the crystallinity, the deposited Y_2O_3 films were investigated, first, by in-situ RHEED and then by GXRD. For GXRD measurements Cu-Kα line (λ=1.5406 Å) was used as an X-ray source and its incidence angle between X-ray beam and substrate plane was 0.2°. Finally to confirm the crystallinity of the films, HRTEM was used. The stoichiometry and chemical bonding state are closely related with the crystallinity. So we

consider the relation with XPS. A 1253.6 eV Mg K-α radition source was used to obtain the chemical state and the stoichiometry of the films and Ar^+ ion as a sputtering gas was used to remove the surface contamination of the film. In order to consider the possible application using Y_2O_3 as a gate insulator, the electrical characteristics were investigated in Al/Y_2O_3(300Å)/p type Si(100) by measurement of I-V and C-V.

In the I-V characteristics, breakdown field strength and leakage current were included. Also, the I-V measurement was performed after the films were oxidized in furnace at temperature of 700℃ for 80min to verify the improvement of breakdown field strength resulting from the formation of interface silicon oxide and defect curing. The C-V characteristic was plotted at 1kHz using HP-4284 system and the dielectric constant of Y_2O_3 was calculated from C-V data.

RESULTS AND DISCUSSION

First, the crystallinity of the deposited film was investigated by in-situ RHEED. Figure 1 shows the RHEED patterns of Y_2O_3 film deposited under the various process conditions. The crystallinity is improved by the increase of substrate temperature. The films deposited at a low temperature below 500℃ show the polycrystalline structure but the phase change to a single crystalline structure occurs by increasing substrate temperature. When the substrate temperature is increased up to 700℃, the film shows the single crystalline structure and the line patterns (d) show that the surface of the film is very smooth.

Second, GXRD measurements were examined and finlally, the crystallinity of the epitaxial growing film was confirmed by TEM analysis. Typical GXRD spectra in Figure 2(a) show that the crystallinity has close dependance on substrate temperature and acceleration voltage. The main peak of Y_2O_3 (222) is gradually sharper and the peak intensity is increased with incresing the acceleration voltage. This tendency is found in figure 2(b). Y_2O_3(222) peak decreases and Y_3O_3 (440) peak newly appears. With increasing the acceleration voltage, Y_2O_3(222) and Y_2O_3 (400) peak is remarkably reduced and Y_2O_3 (440) peak remains. Only Y_2O_3(440) peak is found in acceleration voltage 5kV. These results mean that phase transformation between 500℃ and 700℃ takes place from Y_2O_3(111)//Si(100) to Y_2O_3(110)//Si(100) depending upon the substrate temperature and acceleration voltage.

Figure 3 shows the cross sectional HRTEM image of Y_2O_3 films deposited at acceleration voltage 5 kV and substrate temperature 700

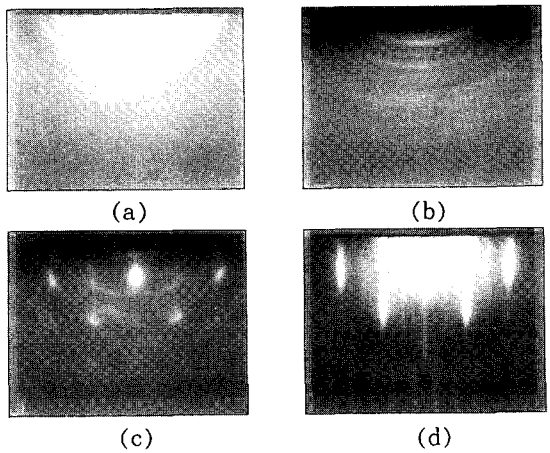

Fig 1. RHEED patterns of Y_2O_3 films deposited at Va=5 kV with a) Ts=300℃, b) Ts=450℃, c) Ts=600℃, d) Ts=700℃. (incident electron beam comes from Si< 100> axis)

℃. As we can anticipate the result from the RHEED and GXRD data, the film is epitaxially grown at above deposition condition and the growing direction of the film is $Y_2O_3(110)//Si(100)$ and $Y_2O_3[110]//Si[100]$. Surprisingly, the interface between Si and Y_2O_3 is very clean and sharp without any other interface oxide layer. While, at low temperature and no acceleration voltage, polycrystalline structure is found and the interface oxide of a very rough layer is in existence Figure 4. These results demonstrate that ICB is adquate technique for epitaxial growing.[12-14]

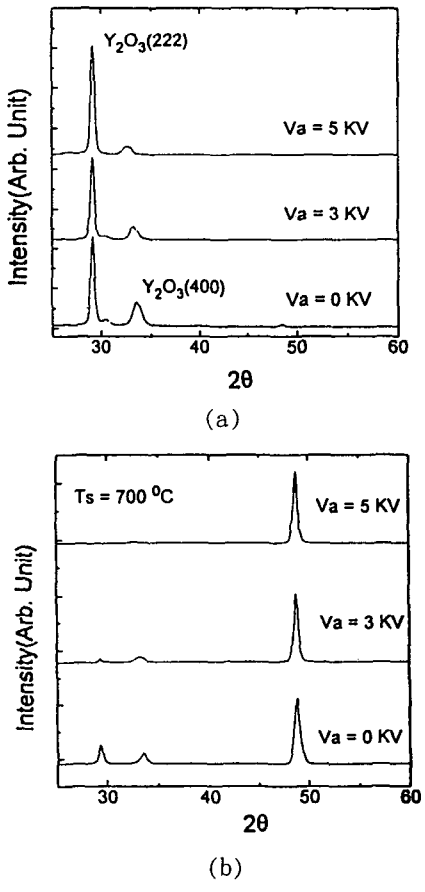

Fig 2. Typical GXRD spectra of 300Å thick Y_2O_3 films deposited at (a) Ts=500℃ and (b) Ts=700℃ with Va=o kV, 3 kV, 5·kV.

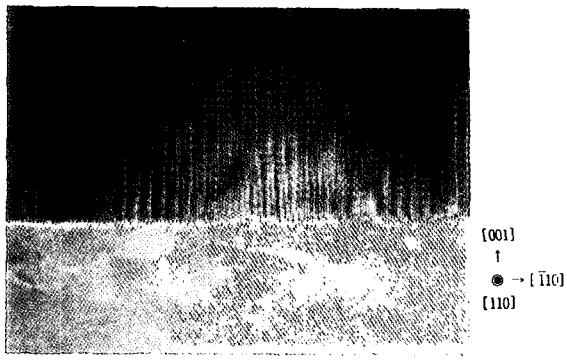

Fig 3. HRTEM image from <110> cross section of Y_2O_3/Si deposited at Ts=700℃ and Va=5 kV

In order to consider the electrical characteristics, $Al/Y_2O_3(300Å)/p\text{-}Si(100)$ MIS structure was fabricated in various substrate temperatures. Figure 5 is the I-V characteristic curve. The leakage current is very high in Y_2O_3 films deposited at substrate temperature of R.T and the breakdown strength of the films has very low value measured as 0.5MV /cm. With increasing the substrate temperature, the leakage currents are remarkably reduced and the breakdown field strength is gradually increased. In the films deposited above substrate temperature 600℃, the breakdown field strength is increased up to 1.2MV/cm, and the leakage current is lower than 1×10^{-8} A/㎠ when applied field is 0.1 MV/cm. After oxidation, the breakdown field strength in the film at 700℃ is increased up to 3.7 MV/cm and the leakage current level is reduced considerably due to the formation of SiO_2 and defect curing.[15]

The defect curing can be explained as follows. The sample deposited at low temperature has many incompletely bonded atom such as Y^0, Y^+, Y^{++}, O and O^+. Thermal annealing prompt these incompletely bonded atom to react. Therefore it reduces the numb-

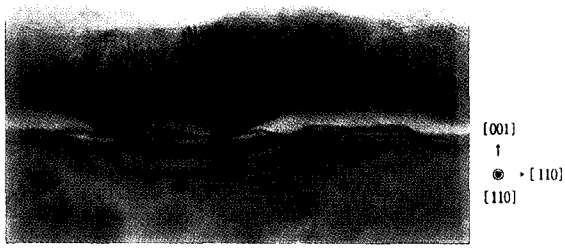

Fig. 4. HRTEM image from <110> cross section of Y_2O_3/Si deposited at Ts=400℃ and Va=0 kV

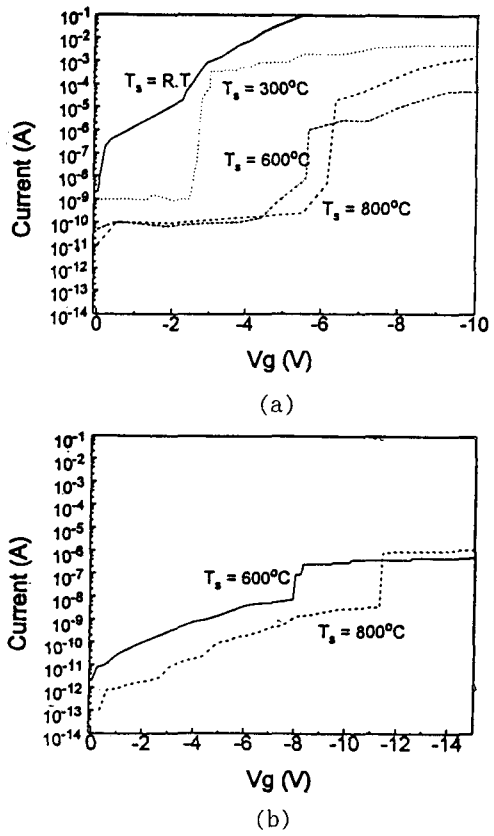

Fig. 5. I-V characteristics of Al/Y_2O_3(300Å)/Si MIS diode structure. a) before oxidation, b) after thermal annealing in oxygen ambience for 80 min

er of vacancies existing inside the thin film. We certified this fact with XPS.

In order to investigate the chemical state of Y_2O_3, XPS was used. The spectra of XPS in Figure 6 represent the photoelectron peaks of O 1s and Y 3d, respectively. In the O 1s peaks, the main peaks indicate the attribution of O^{2-} bonded to Y^{3+} while the sub peaks represent the attribution of physorped O_2 and hydrated O species. In the figure, the multiplet spliting due to spin orbit coupling appears and the peak positions caused by Y $3d_{3/2}$ and Y $3d_{5/2}$ are 158.8 eV and 156.6 eV, respectively.[16] The positions of two peaks in the spectra deviate very much. This indicates that the yttrium atom is not bonded to oxygen atom completely. This spectra also show that as the substrate temperature increases, the number of yttrium atoms bonded to oxygens incompletely decreases. Especially, at the substrate temperature of 700℃, the peak position is coincident with the case of completely bonded yttrium to oxygen. Also, the areal ratio of two peaks, yttrium and oxygen, approaches closely the theoretical value of 1.5 under condition above.

Using the typical C-V measurement, the dielectric constant is calculated from the capacitane of the charge accumulation. The calculated value is $\varepsilon=15.6$, which is about 4 times larger than that of $SiO_2(\varepsilon=3.9)$. If the dielectric constant of SiO_2 is considered, and the thickness of nearly 300Å of Y_2O_3 film is converted to the thickness equivalent to that of SiO_2, then the value of about 75Å can be obtained. Using the thickness of 75Å, the calculated breakdown field is up to about 8MV/cm for breakdown voltage of 6V and up to about 15MV/cm for breakdown voltage of 11.5V after oxidation. These results of electrical characteristics are superior to the other reported results.

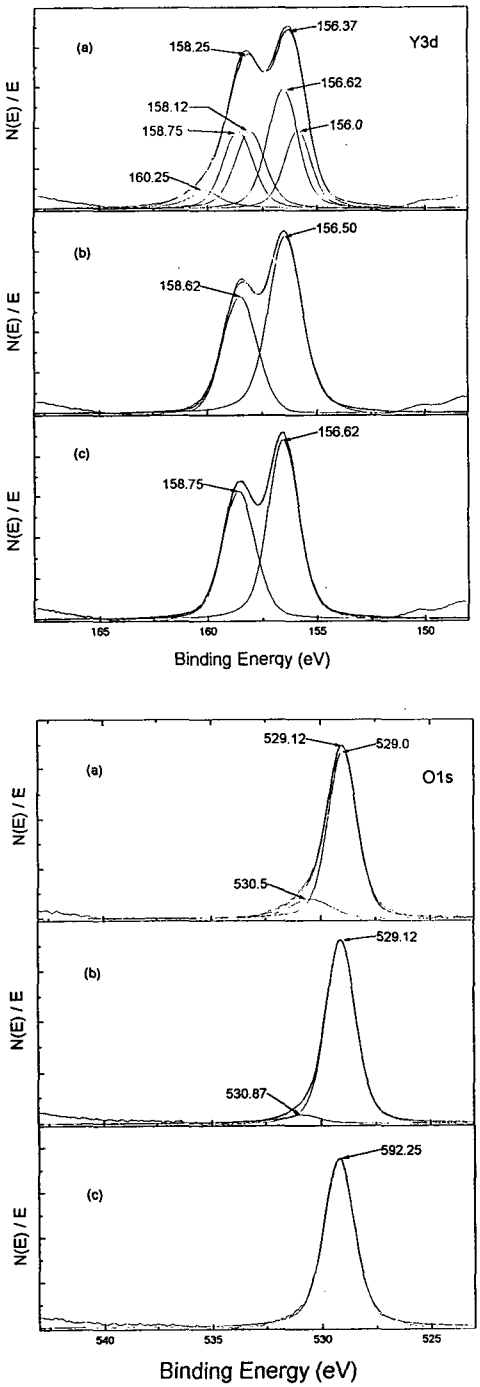

Fig. 6. XPS spectra of core level Y 3d and O 1s with Y_2O_3 films deposited at a) Ts=R.T, Va=5 kV b) Ts=450℃, Va=5 kV and c) Ts=700℃, Va=5 kV.

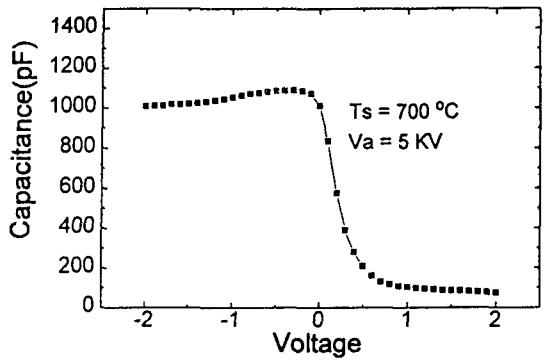

Fig. 7. Typical C-V characteristics of Y_2O_3(300 Å)/Si MIS diode structure.

CONCLUSIONS

Using the r-ICB technique, the Y_2O_3 films were grown on Si(100). As the substrate temperature and the acceleration voltage increase, the phase change from poly crystalline structure to single crystalline structure is observed. At the substrate temperature of 500℃ below and acceleration voltage of 5kV, the growing direction is preferentially oriented to $Y_2O_3(111)//Si(100)$ and at the substrate temperature of 700℃ above and acceleration voltage of 5kV, preferentially oriented to $Y_2O_3(110)//Si(100)$. Under the latter case of condition, it is found that the growing film is epitaxially grown in direction of Y_2O_3 $(110)//Si(100)$. The stoichiometry of the films is also improved in the same condition of improving the crystallinity. From the viewpoint of device application, I-V and C-V characteristics are introduced. The dielectric constant of Y_2O_3 film is calculated to the value of about $=15.6$ using the typical C-V data. The thickness of Y_2O_3 film is converted into eqivalent thickness of SiO_2 at the same capacitance value, and then the breakdown field is calculated by I-V data to 7.5MV/cm

and 14.5MV/cm, respectively without and with oxidation. These results show that the Y_2O_3 is a possible candidate as a future gate insulator in ULSI

ACKNOWLEDGEMENTS

This work was supported by the Korea Science and Engineering Foundation(KOSEF), Samsung Electronics Co., Ltd. and the Basic Science Research Institute Program, Ministry of Education, 1994, Project No. BSRI-95-2426.

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