Impact of Nitrogen Incorporation into Yttrium Oxide on Chemical Bonding Features and Electrical Properties

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Changes in the chemical bonding features and electrical properties of Y_2O_3/SiO_2 stack on Si(100) with post deposition anneal (PDA) in NH_3 ambience at the temperature range of 500-800°C were studied. Comparative studies with PDAs in O_2, N_2 and NF_3 ambiences were made. In NH_3-PDA at temperatures of 600°C and higher, nitrogen incorporation to the dielectric stacks was observed as Si-N-O-Y bonding units. In addition, by 800°C NH_3-PDA, the formation of Si-N-Y bonding units becomes significant, implying that interfacial reactions to form silicate bonds were followed by nitridation. The average nitrogen content in the gate stack was estimated to be 7.4 at.% for 700°C NH_3-PDA and 18.2 at.% for 800°C NH_3-PDA. Capacitance-voltage and current-voltage characteristics of Al-gate metal-insulator-semiconductor (MIS) capacitors show that the NH_3-PDA enables us to reduce the leakage current without a significant decrease in equivalent oxide thickness in comparison to the cases of O_2- and N_2-PDA. We also found that NF_3 anneal after NH_3-PDA is effective to reduce the positive fixed charges in the dielectric stack.
Key words: high-k, X-ray photoelectron spectroscopy, silicate, NH_3 PDA, NF_3 anneal

1. INTRODUCTION

A practical limitation in using conventional silicon oxide or silicon oxynitride as the gate dielectric of metal oxide semiconductor field-effect transistors (MOSFETs) is thought to be its thickness of ~1.5nm due to a high gate leakage current caused by direct tunneling through such an ultrathin gate dielectric. To further scale the gate dielectric thickness down to 1.5nm, metal oxides with dielectric constants (ε_s) higher than SiO_2 have received attention as a potential gate dielectric. Among many candidates to replace conventional SiO_2 and SiON with a high-k gate dielectric, hafnium(Hf)-silicate and Hf-aluminate have received the most intensive study [1, 2]. To decrease electrical oxide thickness, increasing Hf content in the dielectric is preferable. However, from viewpoints of reducing leakage current and securing dielectric reliability, thermal stability against crystallization and phase separation becomes a major concern under a high thermal budget. In a conventional device fabrication process including annealing over 1000°C for source and drain activation, a practical upper limit on hafnium content in silicate or aluminate is placed at 30-40% (ε_s~15-18) at most [3]. To overcome such difficulties, the addition of other elements such as trivalent nitrogen into the dielectric has been studied extensively. Trivalent yttrium has the potential to be an alternative to stabilize the amorphous network in a metal oxide system, considering that yttrium oxide (Y_2O_3) has a crystallization temperature over 900°C, moderate dielectric constant (ε_s~16) more than SiO_2 (ε_s=3.9) and Al_2O_3 (ε_s~9), and favorable energy band offsets [4]. In regards to such physical properties, Y_2O_3 is a promising candidate as an alternative gate dielectric. One of the major research issues for implementation of the Y_2O_3 system is to suppress interfacial reactions to form a silicate layer during post deposition anneal (PDA) [5].

In this work, the influence of NH_3 anneal on chemical bonding structures and the electrical properties of Y_2O_3/SiO_2 stack on Si(100) has been studied by X-ray photoelectron spectroscopy and electrical measurements of Al-gate metal insulator semiconductor (MIS) capacitors.

2. EXPERIMENTAL PROCEDURE

After conventional wet-chemical cleaning steps of p-Si(100), 1-2nm thick SiO_2 layers were grown on pre-cleaned Si(100) at 850°C in dry O_2. Amorphous Y_2O_3 films were formed by electron beam evaporation from a yttrium target under O_2 pressure of 2.5×10^{-5}Pa on $SiO_2/Si(100)$ and followed by PDA in the temperature range from 500 to 800°C in NH_3 (~133Pa, 5 min) ambience. PDAs in O_2 (~1×10^5Pa, 10 sec) and N_2 (~133Pa, 5 min) ambience were also preformed for comparative studies. In addition, NF_3 (~26.6Pa, 1 min) anneal was carried out after NH_3 PDA. Changes in chemical bonding structures in the films with PDAs were measured by X-ray photoelectron spectroscopy using a monochromatized AlKα radiation, in which the photoelectron take-off angle was set at 90°. Electrical properties of the annealed sample were evaluated from the capacitance-voltage (C-V) and current-voltage (I-V) characteristics of Al-gate MIS capacitors.

3. RESULTS AND DISCUSSION

3.1 Chemical Bonding Features in $Y_2O_3/SiO_2/Si$ Stack Structure

Figure 1 shows changes in Si2p, N1s, Y3d and O1s spectra with NH_3-PDA at different temperatures for $Y_2O_3(\sim1.9nm)/SiO_2(\sim2.8nm)/Si(100)$ stack structures. By NH_3 PDA at 500°C, Si2p signals in the higher binding energy side due to Si-O bonding units were decreased, although the signals in the lower binding energy side were increased concurrently, while no N1s signals were observable. This result indicates that Si-O-Y bonds are formed at the interface between yttrium oxide and SiO_2. As NH_3 annealing temperature was increased to 600°C and higher, chemically shifted Si2p signals that peaked at 102eV were significantly increased, accompanied by a significant evolution of N1s signals around 398eV, implying the formation of Si-N bonds in the dielectric network. As for O1s signals consisting of two major components due to Si-O and Y-O bonding units [4], the change in the O1s spectrum with NH_3-PDA at 500°C is explained as a decrease of Si-O-Si bonds peaked at 533eV and an increase of Si-O-Y bonds. For the O1s spectra taken after NH_3 PDA at 600°C and 700°C, an increase in the higher binding energy side suggests the generation of Y-O-N-Si bonding units as a result of an insertion reaction of a N atom into Y-O-Si units. Notice that no change in the Y3d spectrum was detected with N incorporation into Y_2O_3, indicating that N atoms preferentaiallly bond to Si.

Further increase in NH_3-PDA temperature to 800°C causes significant increases in the chemically shifted Si2p signals attributable to Si-N bonds and correspondingly in the N1s signals at $\sim397eV$ as shown in Fig. 2. The result in Fig. 2 indicates the nitridation of the ultrathin interfacial SiO_2 layer and Si(100) surface in conjunction with the generation of Si-N-Y bonds due
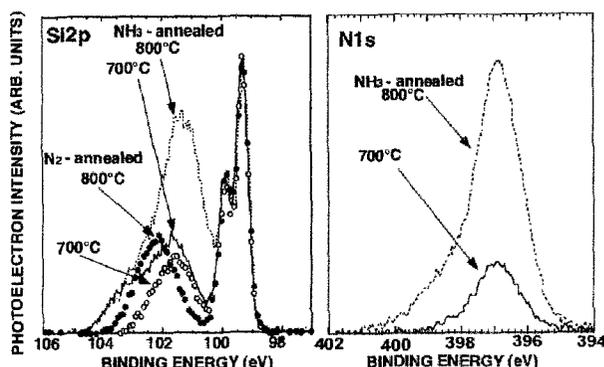

Fig. 2.   Si2p and N1s spectra taken before and after PDA in NH_3 or N_2 ambience of Y_2O_3 $(\sim3.9nm)/SiO_2(\sim0.8nm)/Si(100)$ stacked structures at 700 and 800°C.
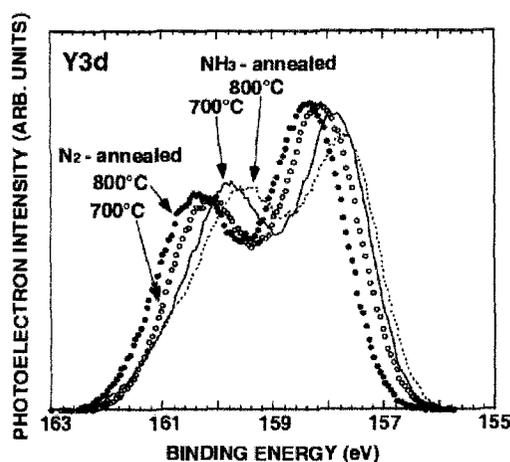

Fig. 3.   Y3d spectra taken before and after PDA in NH_3 or N_2 ambience of $Y_2O_3(\sim3.9nm)/$ $SiO_2(\sim0.8nm)/Si(100)$ stacked structures.
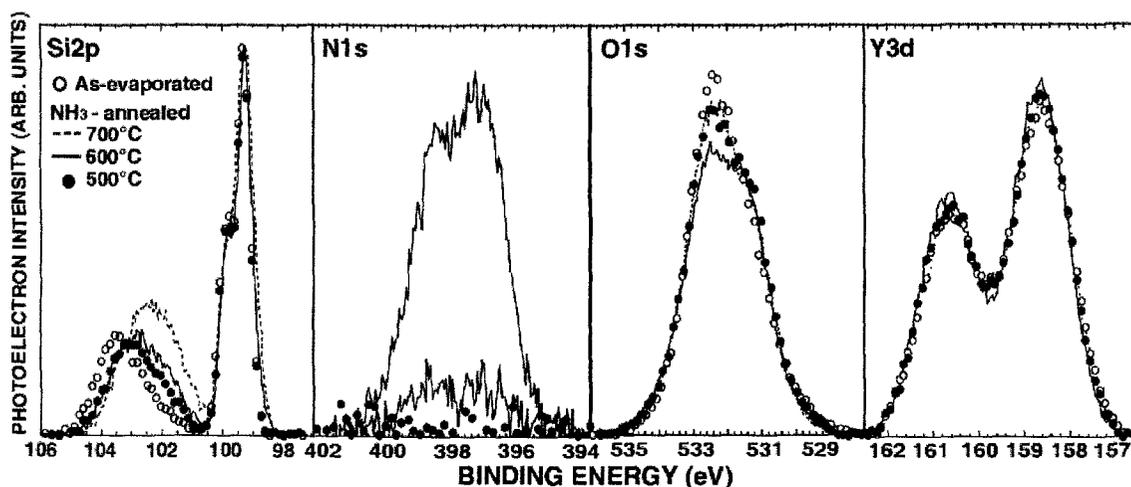

Fig. 1.   Si2p, N1s, Y3d and O1s spectra taken before and after NH_3-PDA of $Y_2O_3(\sim1.9nm)/SiO_2(\sim2.8nm)/Si(100)$ stacked structures, where PDA temperatures were 500, 600 and 700°C.   For Si2p and N1s signals, the binding energy was calibrated with the Si2p3/2 peak at 99.3eV from Si(100) substrate and the spectral intensity was normalized by the Si2p3/2 peak intensity of the substrate signals.   To minimize the influence of the potential drops in the interfacial oxide between the high-k and Si(100) layer on the energy shift of core line signals from the Y_2O_3 top layer, the binding energy for Y3d and O1s spectra was calibrated with the C1s peak at 285.5eV due to carbon contaminants physisorbed on the surface and the spectra intensity was normalized by total Y3d intensity.
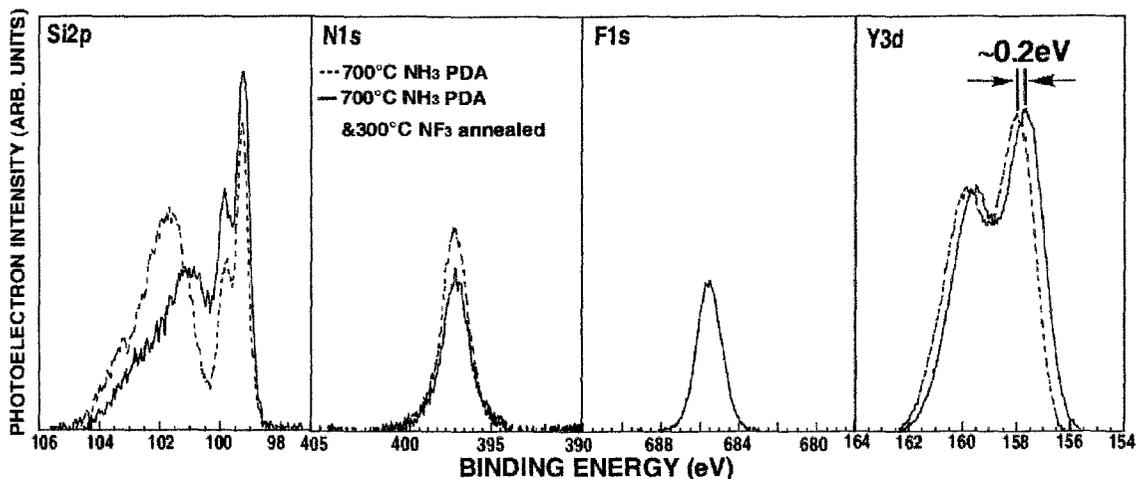
Fig. 4. Si2p, N1s, F1s and Y3d spectra taken after NH_3 PDA at 700°C and followed by NF_3 annealing at 300°C of Y_2O_3(~4.3nm)/SiO_2(~0.9nm)/Si(100) stacked structures. The binding energy was calibrated with the Si2p peak at 285.5eV from carbon contaminants physisorbed on the surface and the spectra intensity was normalized by total Y3d intensity.

to substitution of a N atom for oxygen of Si-O-Y bonds. In fact, the Y3d spectrum is slightly shifted toward the lower binding energy side as a result of the generation of Y-N bonds as shown in Fig. 3. The average N content in the gate stack was estimated to be 18.2at.% for 800°C PDA in NH_3 ambience. After N_2 PDA at 800°C, the chemically shifted Si2p signals due to Si-O bonds were increased in comparison to N_2 PDA at 700°C, being interpreted in terms of the growth of the silicate layer.

When NH_3-PDA at 700°C was followed by NF_3 anneal at 300°C, chemically-shifted Si2p and N1s signals were decreased significantly as represented in Fig. 4. This implies that N atoms in the dielectric stack are efficiently eliminated by NF_3 anneal at a temperature as low as 300°C. From the F1s spectrum after NF_3 anneal, the average fluorine content in the stacks was estimated to be 6.5 at.%. In addition, theY3d spectrum was shifted by ~0.2eV toward the lower binding energy side by NF_3 anneal. The energy shift implies a decrease in positive fixed charges as confirmed later by electrical measurements.

3.2 Electrical Characterization of Al-gate MIS Capacitors with Y_2O_3/SiO_2/Si Stack Structure

The C-V characteristics of Al-gate MIS capacitors for Y_2O_3(~3.9nm)/SiO_2(~0.8nm)/Si gate stacks before and after PDA in NH_3, O_2 and N_2 ambience at 700°C were evaluated by a two-frequency C-V method (50 and 100kHz) as shown in Fig. 5. For the as-evaporated sample, a positive shift in flat-band voltage was observable. On the contrary, the flat-band position of the samples subjected to PDA in NH_3, N_2 or O_2 ambience was shifted toward the negative direction, being consistent with positive fixed charges in the dielectric. A decrease in the accumulation capacitance of the C-V curve measured after PDA in O_2 ambience indicates the growth of the interfacial oxidation layer. After PDA in N_2 ambience, a C-V hysteresis of ~0.3V due to the carrier injection into oxide traps is observed, while no hysteresis was observable in the C-V curve of the film after NH_3 PDA. For the sample subjected to
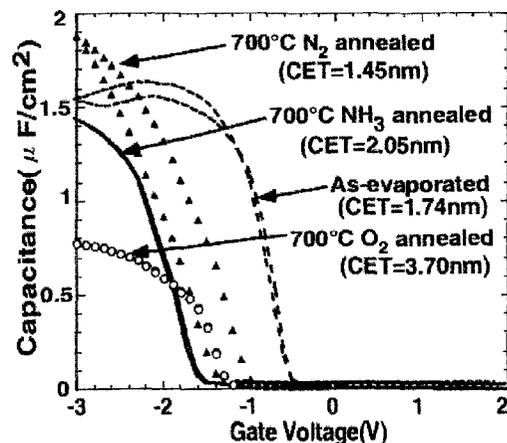

Fig. 5. C-V curves measured before and after PDA in NH_3, N_2 or O_2 ambience of Y_2O_3 (~3.9nm)/SiO_2(~0.8nm)/Si(100) stacked structures.

NH_3 PDA, the net capacitance equivalent thickness (CET) is 2.05nm and the fixed charge density obtained from the flat-band position is ~9.4x.10^{12} cm^{-2}. The I-V characteristics were also evaluated before and after PDA in NH_3, O_2 or N_2 ambience. After NH_3 PDA, the gate leakage current was reduced by ~2 orders of magnitude in comparison with the leakage current through 2nm-thick SiO_2 at an oxide voltage of 1V.

In comparison between the samples subjected to NH_3-PDA at 700°C and subsequent NF_3 anneal at 300°C as shown in Fig. 6, an increase in the CET and a decrease in net positive fixed charges by about 25% were confirmed with NF_3 anneal as expected from the results obtained by XPS measurements, although a C-V hysteresis due to carrier injection was slightly increased. Note that the leakage current level was reduced by a factor of 3.5 at an oxide voltage of 1V even though the CET was decreased by 0.29nm as indicated in Fig. 7.
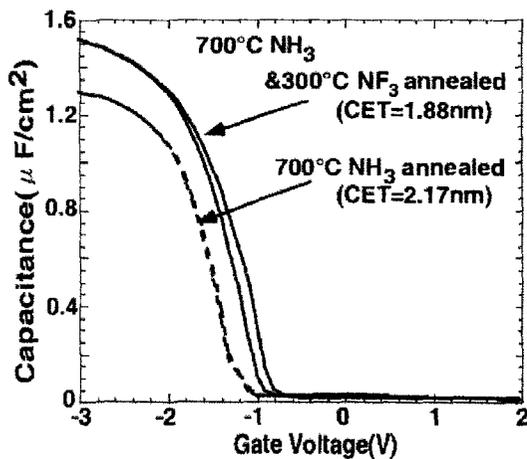
Fig. 6. C-V curves measured after NH_3 PDA at 700°C and followed by NF_3 annealing at 300°C of $Y_2O_3(\sim4.3nm)/SiO_2(\sim0.9nm)/Si(100)$ stacked structures.

Fig. 7. I-V characteristics measured at room temperature for the samples shown in Fig. 6.

4. SUMMARY

Nitrogen incorporation to EB-evaporated Y_2O_3 is promoted by NH_3-PDA at temperatures of 600°C and higher. By 800°C NH_3-PDA, the formation of Si-N-Y bonding units in the dielectic and nitridation of ultrathin interfacial SiO_2 were facilitated. The average N contents in the gate stacks subjected to NH_3-PDA at 700°C and 800°C were obtained to be 7.4 and 18.2 at.%, respectively.

From the C-V and I-V characteristics of Al-gate MIS capacitors, we have confirmed the NH_3-PDA enables us to reduce the leakage current without a significant decrease in equivalent oxide thickness in comparison to the cases of O_2- and N_2-PDA. In addition, we have demonstrated that NF_3 anneal at a temperature as low as 300°C after NH_3-PDA leads us to reduce the nitrogen content in the dielectric stack, positive fixed charges and the leakage current but causes a slight increase in a C-V hysteresis.
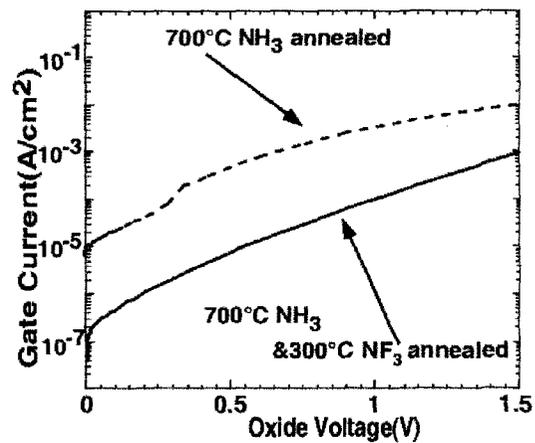
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