Thermal-Stability Improvement of LaON Thin Film Formed Using Nitrogen Radicals

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Abstract

This work reports the influence of nitridation on structural and electrical properties of La_2O_3 gate dielectric films. The issue of La_2O_3 is EOT increase after high temperature post metarization annealing (PMA). To overcome this problem, we incorporated nitrogen in La_2O_3. The EOT increase on the TaN/LaON and W/LaON structure is reduced compared with that on the W/La_2O_3 structure. This is due to nitrogen in LaON and SiN_x-rich interfacial layer which seems to remain after high temperature annealing. W/LaON nMOSFET is also successfully fabricated. Peak electron mobility of 96.2 cm^2/V s was obtained.

Keywords: lanthanum oxide, lanthanum oxynitride, nitrogen radical, EOT, MOSFET

1. Introduction

To further extend the progressive scaling of CMOS devices, gate dielectric thin film has to be replaced by alternative high dielectric constant (high-k) materials. Various metal oxides, for example, HfO_2, ZrO_2, and TiO_2 have been intensively investigated [1]. La_2O_3 has been one of these candidates, due to the high permittivity (ε~27) with large bandgap (~5.5eV). The issue of La_2O_3 is the EOT increase after high temperature annealing. One way to overcome this problem is to add nitrogen to La_2O_3 on the analogy of HfON [2] and HfSiON [3].

In this study, LaON dielectric film with EOT below 1 nm was prepared to evaluate the thermal stability through comparison with La_2O_3. LaON MOSFET was also fabricated.

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2. Experiment

MOS capacitors were fabricated on HF-last n-type Si (100)-oriented wafers (ρ=1~5Ω-cm). La_2O_3 was deposited by E-beam evaporation with nitrogen radicals generated in RF excited nitrogen plasma to form LaON film. Substrate temperature during deposition was set to 300 ^oC. Either tungsten (W) or tantalum nitride (TaN) electrode was deposited *in-situ* by RF sputtering to avoid the strong hygroscopic properties of La_2O_3 [4]. Post Metallization Annealing (PMA) was performed in nitrogen ambient at 300, 500, and 700 ^oC. MOSFET was fabricated on source and drain pre-formed p-type Si, and LaON and metal electrode were deposited afterwards. PMA was performed after that. C-V and J-V measurement with conductance method was used to characterize the MOS capacitors, and Id-Vd, Id-Vg, and split-CV measurement were used for nMOSFET. TEM and X-ray photoelectron spectroscopy (XPS) with monochromatic Al Kα was used for two photoelectron take-off angles (TOAs) to evaluate structure of the gate stack and the chemical bonding of nitrogen, respectively.

3. Results and discussion

Figure 1 shows a cross-sectional TEM image of as-deposited W/LaON/Si sample. A thin interfacial layer is observed between Si substrate and LaON film. From N 1s photoelectron spectra of W(~1nm)/LaON(fig. 1(b)), where the intensity is normalized at the peak around 398 eV. As it is reported that the binding energy of N 1s in Si_3N_4 is 397.3 eV [5], the peak around 398eV implies the formation of SiN_x-rich layer. Considering the electronegativity of oxygen (3.44), which is larger than that of Si (1.90), the high binding energy components may be N-O bond related compound in LaON. Moreover, as these components were found to form above the SiN_x-rich layer, which were revealed by angle-resolved spectra, they were the signals from LaON film. Further investigation should be done to reveal details. It is also observed in Figure 1(c) that the higher binding energy component decreases as PMA temperature increases relatively to that of lower one. This indicates that nitrogen in LaON film move during annealing.

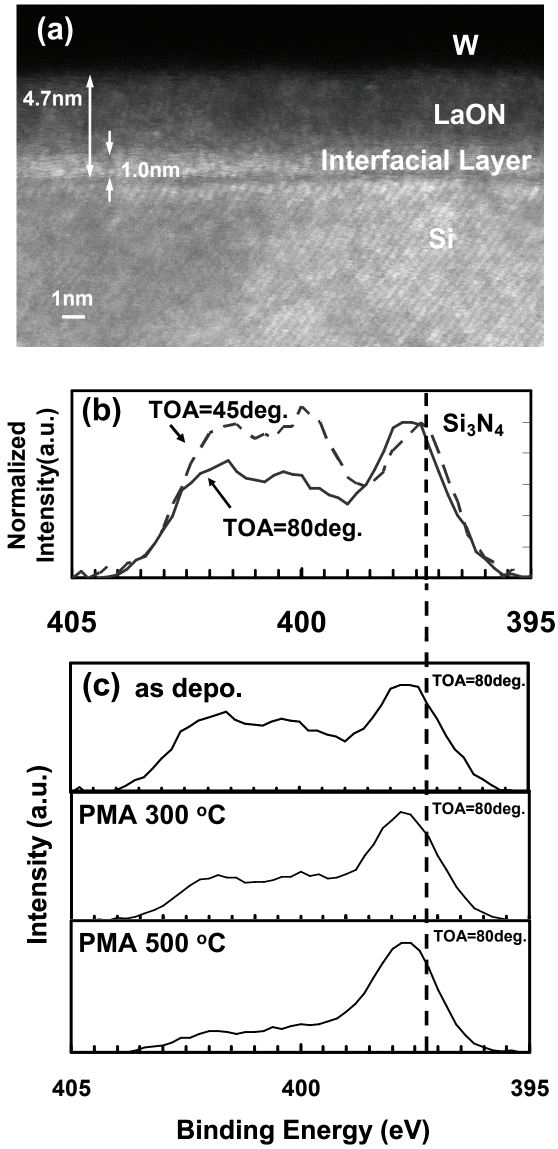

Fig.1. (a) Cross-sectional TEM image of as deposited W/LaON/Si. Interfacial layer was observed between LaON and Si substrate. (b) N 1s spectra of W/LaON/Si normalized at a peak around 397eV. Two components were observed, one is around 397eV, the other is from 399eV to 402eV. (c) N1s spectra of W/LaON/Si as deposited, after PMA300 ^oC and 500 ^oC.

Figure 2 shows the C-V characteristics of W/LaON and TaN/LaON MOS capacitors for different PMA temperatures. W/La_2O_3 MOS capacitor is also shown for reference. EOTs below 1 nm were achieved with both La_2O_3 and LaON film. Hysteresis can be suppressed at high annealing temperature, however, large humps in C-V curves started to appear suggesting the generation of interfacial states.

It is worth noting that nitrogen incorporation can suppress the interfacial state generation at low temperature annealing, as can be seen from the magnitude of humps in C-V curve for PMA 300 °C. D_{it} of W/LaON/Si after PMA 300 °C determined from conductance method was 2.31×10^{12} $cm^{-2}eV^{-1}$, where the D_{it} of W/La_2O_3/Si was 1.17×10^{13} $cm^{-2}eV^{-1}$ at the Si midgap, respectively.

EOT evolution along PMA temperature is shown in fig. 3. It is clear that the EOT increase can be suppressed with LaON film, especially with TaN gate electrode. It is reported that EOT evolution of La_2O_3 at high temperature is caused by generation of lower permittivity interfacial layer [6]. Moreover, it is also reported that nitrogen incorporation into La_2O_3 can suppress the diffusion of Si from substrate [7]. Therefore, we can conclude that nitrogen in LaON suppress the EOT increase. In addition, as the SiN_x-rich interfacial layer remained after high temperature annealing, we speculate that SiN_x-rich interfacial layer also helps suppressing the EOT increase.

It has been reported that W has high oxygen solubility, which result in the formation of interfacial layer [8]. Therefore we believe that TaN has less oxygen than W, and that generation of interfacial layer was suppressed with TaN/LaON. The flatband voltage of capacitors shift to positive direction, except TaN electrode. This can be explained by TaN reduction, which forms Ta metal with small workfunction, resulting negative shift in flatband voltage.

Figure 4 shows the J-EOT plot of W/LaON samples with that of La_2O_3. Characteristics of W/LaON samples before and after PMA 300 °C are similar to W/La_2O_3 film. However, the leakage current of W/LaON sample after PMA 500°C can be suppressed considerably compared to that of W/La_2O_3.

Figure 5(a) shows the Id-Vd characteristics and (b) shows the effective mobility of MOSFET after PMA at 500 °C. D_{it} of the MOSFET determined by

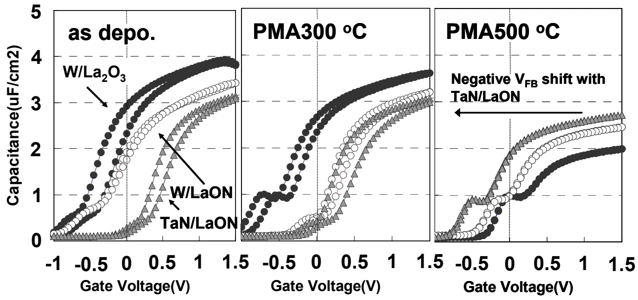

Fig.2 C-V curves of W/La_2O_3/Si, W/LaON/Si and TaN/LaON/Si n-Si MOS capacitors with different annealing temperature measured at 100kHz (A=400μm^2).

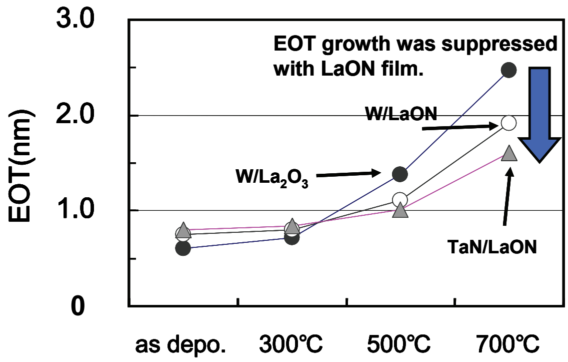

Fig.3. EOT evolution of each sample after PMA. At PMA temperature higher than 500 °C, EOT suppression due to LaON is clearly observed.

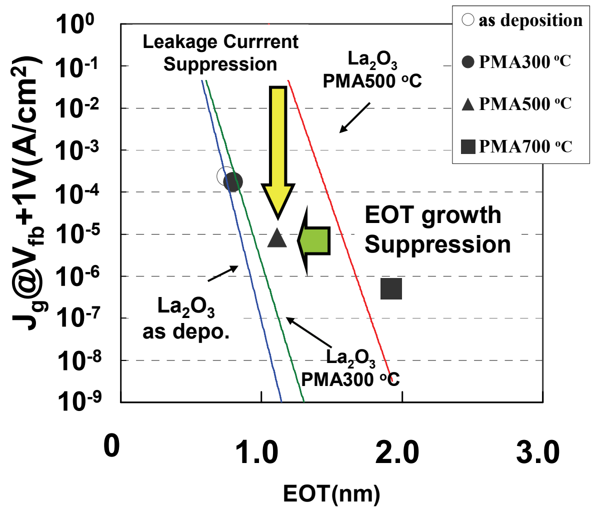

Fig.4. J-EOT plot of W/LaON/Si compared to La_2O_3(line).

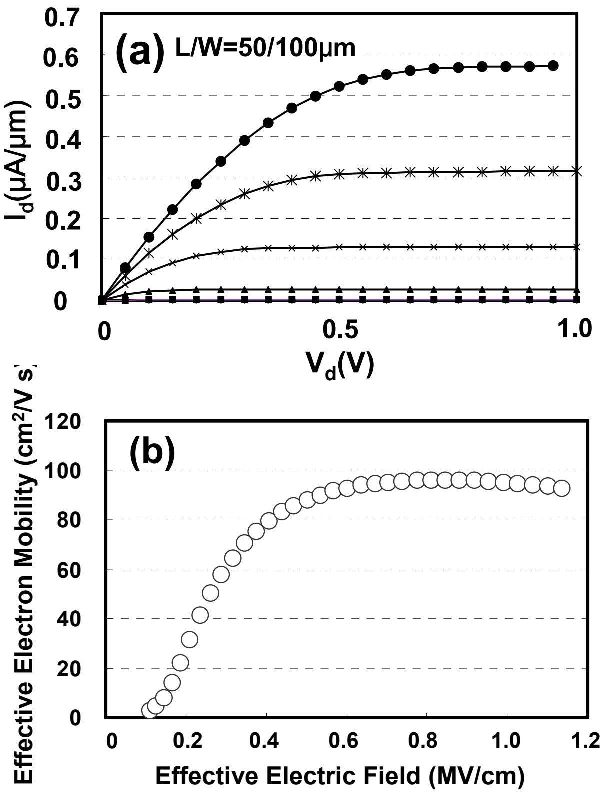

Fig 5. (a) Id-Vd characteristics and (b) effective electron mobility of W/LaON/Si nMOSFET after PMA 500 °C. (EOT = 2.2nm)

the charge pumping was 5.60×10^{12} $cm^{-2}eV^{-1}$. Peak electron mobility was 96.2 cm^2/Vs. Mathew et al. reported that Si surface nitridation before deposition degrades mobility [9]. Another investigation is that as D_{it} increases the effective mobility degrades [10]. The degraded mobility may also be due to large D_{it}. Further process optimization is necessary to improve the interface properties.

3. Conclusion

We have demonstrated the LaON gate stack with W and TaN electrode. Nitridation method employed in this study could suppress EOT increase compared to La_2O_3 film due to nitrogen in LaON and SiN_x-rich interfacial layer. W/LaON nMOSFET was successfully fabricated. Peak electron mobility was 96.2 cm^2/Vs.

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