Quantitative analysis of chemical compositions in ultra-thin oxide–nitride–oxide stacked films having wet oxidized blocking layer

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Abstract

2nd-derivative Auger electron spectra analyses and time-of-flight secondary ion mass spectroscopy depth profiles are employed for analyzing quantitatively chemical compositions in ultra-thin oxide–nitride–oxide (ONO) stacked films. Tunnel oxide of 2.3 nm is grown on silicon substrate in nitrogen-diluted oxygen ambient. Nitride of 5.7 nm is immediately deposited on the tunnel oxide by a low-pressure chemical vapor deposition. Blocking oxide is subsequently grown by oxidizing the oxide–nitride structure in a wet O2 ambient. Some chemical mixing occurs during the ONO formation. That is, the tunnel oxide formed on the silicon substrate changes into SiO1.11N0.67 by nitrogen substitution. Oxygen diffuses into the nitride layer, and converts some of the nitride layer into SiO1.11N0.67 during wet oxidation. We think the SiON and Si2NO species exist near the tunnel oxide–nitride and the nitride-blocking oxide interfaces are segments of the Si2N2O. These are evidence of dangling bonds as unstable chemical species which may act as charge traps in the oxide–nitride interfaces.

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1. Introduction

Oxide–nitride–oxide (ONO) films have been used in the nonvolatile memory devices as charge storage media [1,2]. The concentrations of oxygen and nitrogen as impurities in the nitride and oxide layers, respectively have been correlated with changes in the refractive index, dielectric constants, band-gap, and the charge trapping behaviors of the nitride [3–6]. The chemical compositions of each layer need to be determined precisely because the electrical properties of the dielectric films depend on the chemical composition of each layer in the ONO tri-layer. However, it is very difficult to determine the precise stoichiometry of each layer in the ultra-thin ONO stacked films because of experimental uncertainties due to the surface roughening, the preferential sputtering effect for depth profiles, the different Auger electron escape depth for each element, and the actual interface width [7].

In this study, 2nd-derivative Auger spectrum analysis with Auger electron spectroscopy (AES) and time-of-flight secondary ion mass spectroscopy (ToF SIMS) depth profiles are developed for quantitative analysis of the elemental compositions and the interfacial chemistries in the ultra-thin ONO films.

2. Experimental details

Thick oxynitride samples are prepared for the compositional calibration. Homogeneous films for the compositional calibration are used because of difficulties of determining precise stoichiometries from 2nd-derivative spectra. SiH2Cl2, NH3, and N2O are reacted at 750 °C at a total chamber pressure of \(0.667 \times 10^2\) Pa in a low-pressure chemical vapor deposition (LPCVD) hot-wall reactor to produce 300 nm thick oxynitride films having various oxygen contents. The films are deposited using N2O gas flow rates of 0, 350, 700, and 1400 sccm,
carrying SiH₂Cl₂ and NH₃ in a constant 3.5:1 ratio. Rutherford backscattering spectrometry (RBS) and AES are used to determine the concentrations of Si, N, and O in the oxynitride films as functions of deposition conditions. 2nd-derivative Si LVV Auger spectra are investigated as functions of oxygen content in the films in order to determine standard peak shapes for various compositional oxynitride films. Refractive indices are measured by a spectroscopic ellipsometer.

The ONO samples are prepared on p-type (100) silicon wafers with a resistivity of 13 Ω cm. Silicon wafers are cleaned in boiling H₂SO₄, followed by a HF cleaning process. Oxide of 2.3 nm is grown in an atmospheric-pressure nitrogen-diluted oxygen ambient (O₂:N₂ = 7.25 ℓ/min:7.75 ℓ/min) at 800 °C. Nitride of 5.7 nm is deposited by a LPCVD using dichlorosilane (SiH₂Cl₂) of 30 sccm and ammonia (NH₃) of 100 sccm as precursors at 785 °C. The nitride film is oxidized in an atmospheric-pressure wet O₂ ambient at 900 °C for 67 min.

For the compositional profiles in the ultra-thin ONO layers, the effects of surface roughening, ion beam mixing, and information depth are deconvoluted by using standard techniques [7]. The AES analyses are performed in a PHI 4300 SAM apparatus working at a base pressure of 2.7 × 10⁻⁷ Pa, equipped with an electron beam source of 2 kV, 200 nA, and Ar⁺ ion gun. The energy scale of AES apparatus is calibrated using a flat, fine-grained Cu sample that has been etched to remove surface contamination by an ion sputter. As a result, the first derivative Si LVV negative peak energy is analyzed to 96.0 eV in silicon substrate. Sputtering is performed in wide area (3 × 3 mm²) rastering, low sputtering angle (20°), Zalar rotation™, and quite low ion energy (1.5 keV) in order to minimize preferential sputtering and bonding damage in depth profile determination. It is known that the high ion beam energies and angles may change the compositions and Si LVV peak shapes [8].

ToF SIMS profiles are used to corroborate AES profiles, and cross-sectional transmission electron microscopy (XTEM) is used to determine the thickness of each layer in the ONO films. ToF SIMS depth profiles are obtained by using a CAMECA ION-ToF instrument. Cs⁺ primary ion beam of 1.0 keV is rastered over 200 × 200 μm² area. Secondary ions are extracted and analyzed from the central 60 μm diameter area of the crater using argon ion gun of 10 keV. In this way, it is possible to use a very low sputtering rate for a high depth profile resolution while minimizing the secondary effects of sputtering, like ion beam mixing of nitrogen.

3. Results and discussion

Fig. 1 shows the atomic concentrations and the refractive indices of oxynitride films as functions of N₂O gas flow rate.

![Fig. 1. Atomic concentrations and refractive indices of the oxynitride films as functions of N₂O gas ratio.](image)

![Fig. 2. Auger profiles of various standard oxynitride films; (A) original Auger spectra and (B) 2nd-derivative Si LVV Auger spectra. The spectra in the figures are vertically shifted relative to the y-axis.](image)
The atomic concentration of oxygen increases from 0% to 35% as N2O flow rates increase from 0 sccm to 1400 sccm. However, the nitrogen contents decrease from 55.2% to 28%, and refractive indices also decrease as N2O gas flow rate increases.

Fig. 2 shows (A) original Auger spectra and (B) 2nd-derivative Si LVV Auger spectra of the various standard oxynitride films. The compositions of the films have been determined independently from RBS observations.

It is common practice to collect and present AES data in the first-derivative mode. Background signals can be removed and the visibility of overlapping peaks can be enhanced by differentiation of the original Auger spectra. 2nd-derivative spectra have been used for finding quickly and easily locations of peak positions. In 2nd-derivative spectra of Fig. 2(B), negative peaks occur at approximately middle position between the overlapped peaks in the original spectra [9].

As shown in 2nd-derivative AES spectra of oxynitride films that have various stoichiometries in Fig. 2(B), the negative peak (Si–O at 76.5 eV) of SiO2 shifts toward the positive direction with increasing the nitrogen content of the film, and the negative peak (Si–N at 84.5 eV) of SiN1.23 shifts toward the negative direction with increasing the oxygen content of the film. The peak at 94.5 eV is attributed to elemental silicon. The peaks in the Auger kinetic energy range of 90–92 eV are thought to occur due to the damaged layer, silicon nonbonding state, and excess silicon.

Fig. 3 shows the Auger kinetic energy as a function of O/(O+N) ratio in the 2nd-derivative Auger Si LVV spectra obtained from the silicon oxynitride films.

Si–O–Si + NH3 ⇌ SiNH2 + SiOH  
(1)

SiNH2 + SiOH ⇌ Si2NH + H2O  
(2)

and

2SiNH2 + 2SiOH ⇌ 2Si2NO + 3H2  
(3)

Fig. 4 shows the 2nd-derivative Auger Si LVV spectra of various layers during formation of the ONO tri-layer.

In order to analyze quantitatively the concentrations of oxygen and nitrogen in the ultra-thin ONO films, we compare the Si LVV line shapes obtained from the various oxynitride films with the 2nd-derivative Auger Si LVV spectra obtained from various film structures during formation of the ONO films. Fig. 4 (a) shows a typical spectrum of the tunnel oxides prior to nitride deposition. A spectrum of the oxide–nitride obtained after nitride deposition is shown in Fig. 4(b). The Si LVV peak of 76.5 eV for SiO2 shifts to 80.0 eV, and decreases in intensity after nitride deposition. Position shift and intensity change of the peak occur during the formation of silicon oxynitride compounds because of the reactions between the tunnel oxide and the nitrogen in NH3 gas. During nitride deposition, NH3 and its decomposition products react with the nitride as follows [10];

Fig. 4 (c) shows a deep minimum peak and a second peak at 84.5 eV and 91.0 eV respectively, as a spectrum obtained from the relatively thick 5.7 nm nitride layer. Both peaks show characteristics of amorphous nitride films. The second peak at 91.0 eV is associated with silicon dangling bonds or excess silicon in the nitride film. The silicon dangling bonds are believed to be responsible for shallow traps within the bandgap of the nitride. During subsequent oxidation of the nitride film at 900 °C in wet O2, the Si LVV peak at 84.5 eV shown in Fig. 4 (c) shifts to 91.0 eV.
83.5 eV as shown in Fig. 4(d). The intensity of the small Si signal at 91.0 eV decreases during oxidation of the nitride film. It suggests that oxygen diffused into the nitride passivates the shallow traps in the nitride near the blocking oxide. Therefore, charge carriers injected into the nitride are stored in deep traps of the nitride, and memory characteristics of polysilicon–oxide–nitride–oxide–silicon (SONOS) devices are improved as compared with those of metal–nitride–oxide-semiconductor devices [10–12].

Fig. 5 shows a high-resolution XTEM image of the ultra-thin ONO structure. The oxide adjacent to the crystalline silicon substrate is called the tunnel oxide since the charge carriers tunnel from the silicon surface through this layer into the nitride layer where they are stored in deep traps. The top oxide is named the blocking oxide because it blocks charge injection from the gate electrode into the nitride. The thicknesses of blocking oxide, nitride and tunnel oxide are 4.0 nm, 3.3 nm and 2.3 nm respectively, and constant within a few percentage. The nitride thickness is reduced from as-deposited 5.7 nm to 3.3 nm due to thermal oxidation for growing the blocking oxide. The XTEM image suggests well-defined interfaces between oxides and nitrides. That is, the background contrast at those points is fairly abrupt and discontinuous.

Fig. 6 shows the AES depth profiles of the ONO samples composed of 2.3 nm tunnel oxide, 3.3 nm nitride, and 4.0 nm blocking oxide. Sensitivity factors of Si, N, and O for calculating quantitatively composition of the ONO samples are decided using the SiO\textsubscript{0.79}N\textsubscript{0.84} reference sample confirmed stoichiometrically by RBS analysis.

It is shown that a chemical composition in the interfaces between the oxides and the nitride layer is gradually changed in the ultra-thin ONO films, even though the XTEM image shows well-defined interfaces between the oxides and the nitride. Clearly, some of these gradual variations must come from an imperfect depth resolution. First, there are always some variations in sputter rate due to micro roughness and a difference of elemental bonding strength. This will tend to blur the interfaces. Second, there is a finite escape depth for the Auger electrons and also electron backscattering [13]. The most definite inconsistency at stoichiometry analysis of stacked 2–5 nm super thin film is caused by information depth differences of Auger electrons in each element, because escape depth from material increases in elements that have higher AES kinetic energy.

Fig. 7 shows results of linear least-squares (LLS) fit that come from various AES peak energies of 2nd-derivative Si LVV spectrum.

The LLS fit is essential for analyzing thin layers such as nitrides, oxides, and oxynitrides. This analysis is based on the 2nd-derivative Auger kinetic energies of Si LVV. First of all, montages of all Si LVV Auger spectra are made from the AES depth profiles of Fig. 6, and representative spectra from each layer of the ONO films are selected. Values of negative peak energy of the representative spectra are 80.0 eV for the tunnel oxide film, 83.5 eV for nitride film, 76.5 eV for blocking oxide, and 94.5 eV for silicon substrate. And then, these 4 representative Auger...
spectra are compared with all Si LVV spectra of the ONO thin films. As shown in Fig. 7, the silicon nitride film has a little oxygen (83.5 eV, SiO$_{0.27}$N$_{1.09}$) that comes from wet oxidation process for growing the blocking oxide. Based on this LLS fit, the chemical compositions of the ONO films are analyzed as follows; Pure SiO$_2$ (76.5 eV) is essentially present at the upper surface of the blocking oxide, the SiO$_{1.11}$N$_{0.67}$ (80.0 eV) is mainly distributed in the near blocking oxide–nitride interface and the tunnel oxide. The SiO$_{1.11}$N$_{0.67}$ signal shows that nitrogen penetrates all the way through the tunnel oxide and approximately 2.0 nm into the blocking oxide. It is consistent with the results reported by Minami et al. [14].

Fig. 8 shows the ToF SIMS depth profiles of the ultra-thin ONO films.

The SiO$_3$ species suggests that the SiO$_2$ is most present in the blocking oxide and tunnel oxide. The maximum of the oxygen signal in the tunnel oxide is equal to that in the blocking oxide, but the SiO$_3$ peak in the tunnel oxide is lower than that in the blocking oxide. It is apparently shown that pure Si–O bonding is decreased in the tunnel oxide, but Si–N bonding is increased by NH$_3$ gas during the deposition of nitride. Chemical reaction between the tunnel oxide and NH$_3$ gas follows Eq. (3). As a result of it, a lot of Si$_2$NO phases exist in tunnel oxide.

The SiON and Si$_2$NO species come from desorption of various SiO$_x$N$_y$ oxynitride bonds that exist as an intermediate phase between the SiO$_2$ and the Si$_3$N$_4$ in the ToF SIMS analysis for the ultra-thin ONO films. Most complete molecular constituents are detached by driving the accelerated sputtering ion and primary ion of ToF SIMS. However, a form of the complete distribution could be derived directly from the distribution of the respective quasi-molecular ions. So, we think the SiON and Si$_2$NO species are segments of the Si$_3$N$_4$O that can exist in the silicon oxide–silicon nitride interfaces [15]. The Si$_3$N$_4$ and the SiO$_2$ phases never

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**Fig. 8.** ToF SIMS depth profiles of the ultra-thin ONO films.

**Fig. 9.** (A) The atomic bonding structures of the Si$_2$N$_2$O and (B) various dangling bonds in the oxynitride.
coexist in the bulk under equilibrium conditions. They are always separated by the silicon oxynitride, Si$_2$N$_2$O. Fig. 9 (A) shows atomic bonding structure of the Si$_2$N$_2$O. A region of the Si$_2$N$_2$O phase that exists at the silicon nitride–silicon oxide interface is very narrow. So near interface region has a lot of defects in phase transformation process. Fig. 9 (B) shows various dangling bonds in the oxynitride. They may be thought of as origins of the charge traps in these interfaces and silicon nitride regions [16]. We think these charge traps are caused by various dangling bonds of the Si$_2$N$_2$O, and are extremely important for understanding the memory characterizations of the SONOS devices.

4. Conclusions

The chemical structures and origin of memory traps in the ultra-thin ONO films have been investigated. 2nd-derivative Auger Si LVV spectra and Auger depth profiles are used to determine the oxygen and nitrogen profiles in the ONO tri-layer. ToF SIMS has been used to determine the combined chemical nature of the ONO structure. These techniques provide insight into the chemical bonding states in the ultra-thin ONO films. The SiON and Si$_2$NO chemical species represent the presence of various dangling bonds by segment of the Si$_2$N$_2$O near oxide–nitride interfaces. They may be thought of as origins of the charge trapping sites in the oxide–nitride interfaces.

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