

Characterization of Stoichiometric ZrO₂ Thin Film on Si by Angle-Resolved X-ray Photoelectron Spectroscopy

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Abstract. Simultaneous thermal oxidation and nitridation technique was utilized to transform sputtered Zr to stoichiometric ZrO₂ thin films on Si substrate. The stoichiometry of this type of oxide has high dielectric constant value of ~25 may be applied as dielectric in metal-oxide-semiconductor-based power devices. Through nitrous oxide gas environment, the oxidation/nitridation process was performed at 700°C for a set of time of 5–20 min. Chemical properties of the fabricated films have been characterized by angle-resolved x-ray photoelectron spectrometer. From the characterization, it was found that stoichiometric Zr-O (ZrO₂) was formed. Nitrogen content in the samples was investigated. It was identified that sample oxidized/nitrided for 15 min gives the highest atomic percentage of nitrogen of 2.64 at% in the interfacial layer. This nitrogen content in the near interface region may help to passivate the Si dangling bonds, which may thus enhance the interface quality of oxide-semiconductor.

Introduction

Aggressive downscaling of microelectronic devices based on Si substrate has urged drastic reduction of the thickness of gate dielectric and search of new dielectric materials with high dielectric constant in order to attain low leakage current [1-4]. Several high dielectric constant (k) oxides have been studied nowadays and ZrO₂-based compounds may be considered as one of the most promising materials for the future generation nodes due to its sufficiently high κ value (22–25), suitably large bandgap (5.8–7.8 eV), good thermodynamic stability when in contact with Si up to ~900°C of processing temperature, minimal lattice mismatch with Si(100), and easily stabilized in the form of cubic or tetragonal polymorphs, which may further improve its effective κ value.¹⁻⁴

Different deposition technique will determine the quality of the ZrO₂ thin film.³ According to the previous reports, stoichiometric ZrO₂ thin films were successfully produced by sputtering of metallic Zr followed by thermal oxidation in O₂ environment.^{3, 5-7} However, due to the diffusion and reaction between oxygen, silicon, and zirconium, an undesirable interfacial layer (IL) was unavoidably formed in between ZrO₂ and Si, which reduces the capacitance, thus degrading the performance of the MOS capacitor. Hence, the IL thickness in between ZrO₂ and Si must be reduced. Incorporation of nitrogen in the film is a possible solution. Film contented with nitrogen may help to suppress the out-diffusion of Si by passivating the dangling bonds of Si surface and improve the hot carrier resistance at the Si-dielectric interface.⁸⁻¹⁰ Based on the literatures, a nitrogen-incorporated ZrO₂ film has shown encouraging electrical characteristics.¹⁰⁻¹² In order to perform oxidation and nitridation simultaneously, NO and N₂O are the typical gases used.⁸ Comparatively, N₂O is more appropriate and preferable to be used owing to its non-toxic property.¹³

In our previous reports,¹⁴⁻¹⁶ detailed analyses of structural, chemical, and electrical properties of simultaneously oxidized and nitrided sputtered Zr thin film on Si in N₂O ambient have been studied. The X-ray photoelectron spectroscopy (XPS) analysis has provided the information about the chemistry of the layers and interfaces in presence. Particularly, it has revealed that a stoichiometric ZrO₂ film has been formed along with IL of ZrSiON and its related compounds. The thickness of IL was depending on the oxidation/nitridation time. However, there is no report on characterization of simultaneously oxidized and nitrided sputtered Zr thin film on Si using angle-resolved XPS or ARXPS. This technique offers non-destructive analysis at near-normal electron emission angles without the need to remove any material. Therefore, the purpose of this paper is to report the additional information about the distribution of materials within the layer using ARXPS and to compare the information obtained from XPS analysis in the previous report.

Experimental details

n-type Si(100) wafers (1-10 Ω-cm) were subjected to an ultrasonic cleaning, followed by a standard RCA cleaning method and then treated with a diluted HF solution (1 HF : 50 H₂O) for 15 s to remove native oxide from the surface prior to Zr metal sputtering. Edwards Auto 500 RF sputtering system was used to deposit an ultrathin 5-nm Zr metal thin film on the cleaned Si substrates by using a Zr metal target (Alfa Aesar, 99.5%). RF power, working pressure, inert Ar gas flow, and deposition rate were configured at 170 W, 1.2×10⁻⁷ Torr, 20 cm³/min, and 2 Å/s respectively. Thermal oxidation and nitridation was performed simultaneously after the deposition. Samples were placed into a horizontal tube furnace and heated up from room temperature to 700°C at a constant heating rate of 10 °C/min in an Ar flow ambient. Once the set temperature was reached, N₂O gas was then introduced with a flow rate of 150 mL/min for a set of durations (5, 10, 15, and 20 min). Samples were eventually taken out at room temperature after the furnace was cooled down to room temperature in an Ar ambient.

The ARXPS data were collected using a Kratos Axis UltraDLD equipped with a hemispherical electron energy analyzer. Spectra were excited using monochromatic Al K_α X-rays (hν = 1486.69 eV) with the X-ray source operating at 150 W. This instrument illuminates a large area on the surface and then uses a hybrid magnetic and electrostatic lens system to collect photoelectrons from a desired location on the surface. The analysis area was approximately a 300×700 μm² spot (hybrid/slot). The ARXPS data were reported as a function of take off angle (with respect to the surface normal). Thus normal emission (least surface sensitive) with the sample lying in the horizontal plane is 0°. The subsequent measurements at 20° increments thus become more surface sensitive with the final set of spectra taken at 80° take off angle being most sensitive to the sample surface. The measurements were carried out in normal emission geometry. Survey scans were collected with 160 eV pass energy, whilst core level scans were collected with pass energy of 20 eV. The analysis chamber was at pressures in the 10⁻⁹ torr range throughout the data collection for the ARXPS measurements. The recorded C 1s peak due to the adventitious carbon-based contaminant on the surface, with respect to the literature value of 284.6 eV,^{17, 18} was used as a reference to compensate for the charging effect of the XPS spectra. Surface charge and linear background were corrected with the help of CasaXPS software (version 2.3.15) before deconvolution of the XPS spectra was performed. The total concentration of an element (C_x) available in the investigated films was calculated based on the following equation:¹⁹⁻²¹

$$C_x = \frac{I_x/S_x}{\sum_i I_i/S_i} \times 100 \quad (1)$$

where, I_x and I_i were peak intensity of the evaluated element and all other detected elements, respectively. S_x and S_i were sensitivity factor of the respective evaluated element and all other detectable elements. The sensitivity factor is dependent on XPS system. In this work, the sensitivity factors for Zr 3d, Si 2p, O 1s, N 1s, and C 1s were 2.576, 0.328, 0.78, 0.47, and 0.278, respectively.

Results and discussion

As recorded by wide scan of ARXPS, core-level spectra of Zr 3*d*, Si 2*p*, O 1*s*, and N 1*s* have been detected in all oxidized samples. Then narrow scan was performed for each element. Typical narrow scans of each core-level spectrum as a function of resolving angle for all oxidation durations are presented in Figs. 1–4. A non-linear Gaussian-Lorentzian function (solid lines) was used to deconvolute the measured peaks (open circles) using CasaXPS software (version 2.3.15). The Zr 3*d* spectra (Fig. 1) are well fitted by Zr-O at their respective binding energies. Zr 3*d* doublet, which corresponds to 3*d*_{5/2} and 3*d*_{3/2} spin-orbit split components at 184.4 and 182.0 eV, respectively, has been detected at the top-most surface (resolving angle of 60–80°) for all oxidized samples (5–20 min). This indicates that stoichiometric Zr-O (ZrO₂) is formed.²² As the resolving angle decreases, a progressive chemical shift of Zr-O peaks towards a lower binding energy has been observed. This is due to evolution from stoichiometric to sub-stoichiometric Zr-O towards a deeper region of all investigated films.^{23, 24} By using this non-destructive ARXPS technique, it is found that Zr-N and Zr-Si-O peaks were not detectable, as compared to the destructive XPS technique, which was previously reported in Ref. 14. This may be due to the minute amount of Zr-N and Zr-Si-O in the analysis volume of ARXPS technique.

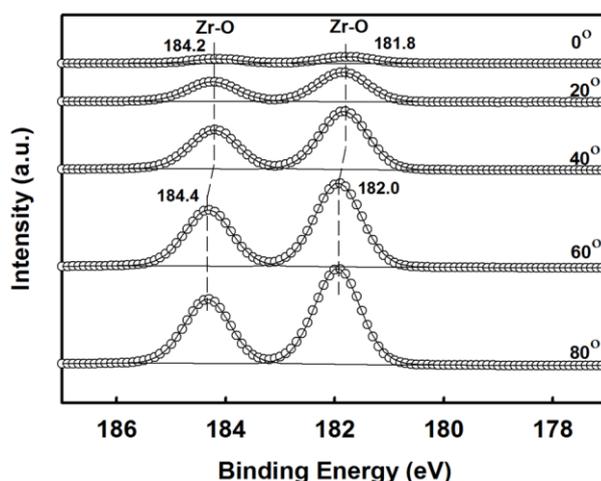


Fig. 1: Typical Zr 3*d* core level XPS spectrum as a function of resolving angle for oxidized/nitrided samples (5–20 min).

Typical Si 2*p* spectra (Fig. 2) were studied in order to further identify and verify existence of other components in the oxidized samples. At the top-most surface (resolving angle of 60–80°), there is no observable peak for all investigated samples. As the resolving angle decreases, Si-O-N and Si-N were detected at binding energies of 101.6 eV^{19, 21} and 99.9 eV,²¹ respectively. This can be inferred that Si-O-N and Si-N are the possible compounds near and/or in the interfacial layer of the investigated samples. The detection of these peaks in Si 2*p* spectra is in consistence to the results shown in the previous report.¹⁴

Analysis of typical O 1*s* spectra (Fig. 3) is of interest as it depicts information, which was obtained earlier. At the top-most surface (resolving angle of 60–80°) of all investigated films, two peaks can be fitted in the O 1*s* core level spectra. The peaks located at 530.0 eV²⁵ and 532.0 eV²⁶ are associated to stoichiometric Zr-O. Identical to the observation made in Zr 3*d* spectra (Fig. 1), the O 1*s* spectra has a progressive chemical shift towards lower binding energies. This is supported by the earlier claim (Fig. 1) that sub-stoichiometric Zr-O is detectable as it moves deeper inside. With decreasing of resolving angle, Si-O-N (531.5 eV¹⁹) is detected in all oxidized samples. This is in agreement with the observation being obtained in Si 2*p* spectra (Fig. 2). Coincidentally, this peak (531.5 eV) is overlapping with Zr-O that is chemically shifted due to non-stoichiometry.

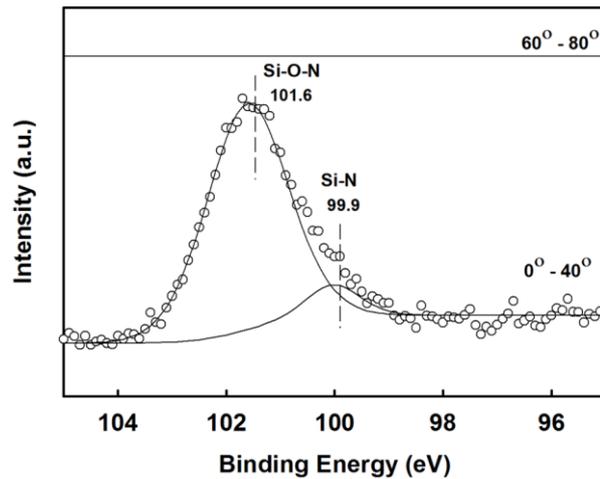


Fig. 2: Typical Si $2p$ core level XPS spectrum as a function of resolving angle for oxidized/nitrided samples (5–20 min).

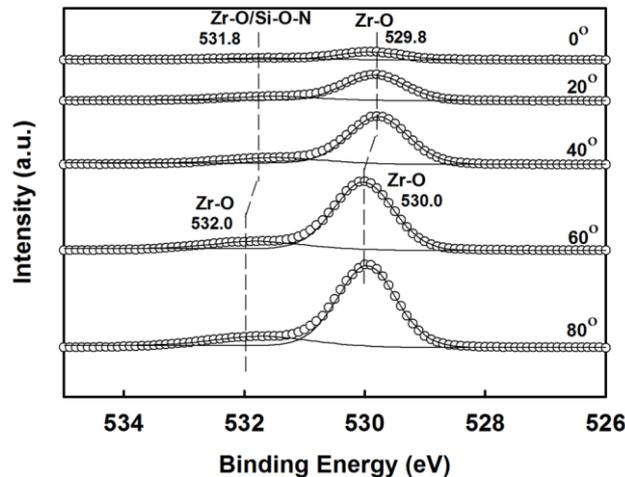


Fig. 3: Typical O $1s$ core level XPS spectrum as a function of resolving angle for oxidized/nitrided samples (5–20 min).

Typical narrow scan of N $1s$ core level spectra is presented in Fig. 4. There is no peak being detected at higher resolving angles of $60\text{--}80^\circ$. With the decrement of resolving angle, a peak at binding energy at 398.3 eV is detected in all samples. This peak is associated with Si-O-N.¹⁹ Again, this conclusion is in agreement with the analysis obtained from Si $2p$ spectra (Fig. 2). Si-N (397.0 eV ¹⁹) is another detected compound in all investigated samples.

Distribution of nitrogen in terms of broadness, maximum atomic percent, and its location vary with samples.¹⁴ Fig. 5 shows the atomic percentage of nitrogen in the interfacial layer for different oxidation/nitridation duration samples (5–20 min). It is found that sample oxidized for 5 min reveals the highest atomic percent (8.45 at%) of nitrogen. In the previous report,¹⁴ by using destructive XPS characterization technique, the detected nitrogen concentration is in the range of 18 to 19% and it is consistently detected even more than 3000 s of etching time. With both observations, it may again hypothesize that nitrogen is embedded deep into the Si substrate. This may be due to the high diffusion rate of nitrogen at 5 min oxidation/nitridation duration. However, this type of distribution does not observe for other oxidized samples (10–20 min). In these samples, nitrogen is accumulated at the interfacial layer with concentration of 0.62–2.64 at%, which is much lower than the concentration detected in 5-min oxidized sample. Among the three oxidized samples (10, 15, and 20 min), 15-min oxidized sample demonstrates the highest concentration of nitrogen (2.64 at%). For 10- and 20-min oxidized samples, concentration of nitrogen is 0.62 and 0.71 at%,

respectively. This is in line with the trend of IL thickness with 15-min oxidized sample showing the thinnest layer in the previous report.¹⁴ Hence, this can be inferred that nitrogen content in the near interface region may help to passivate the Si dangling bonds, which may thus enhance the interface quality of oxide-semiconductor.

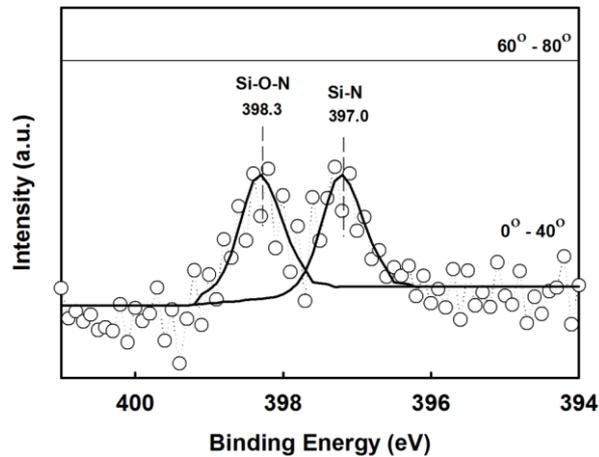


Fig. 4: Typical N 1s core level XPS spectrum as a function of resolving angle for oxidized/nitrided samples (5–20 min).

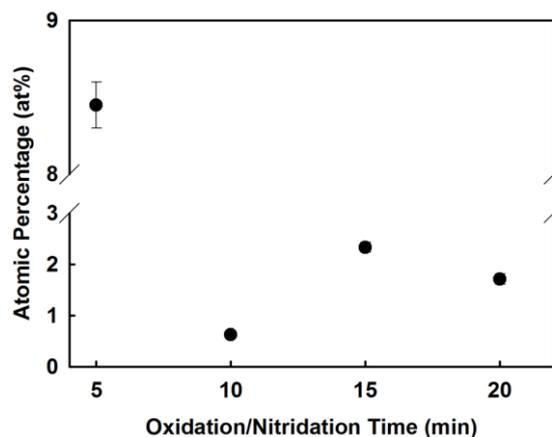


Fig. 5: Atomic percentage of nitrogen in the interfacial layer for different oxidation/nitridation duration samples (5–20 min). The error bars indicate the maximum and minimum atomic percentage of nitrogen in the interfacial layer.

Conclusion

In this work, chemical properties of sputtered Zr oxidized in N_2O ambient for different oxidation durations (5–20 min) were presented. From the ARXPS results, it was found that stoichiometric Zr-O (ZrO_2) was formed. Nitrogen content in the samples was investigated. It was identified that sample oxidized/nitrided for 15 min gives the highest atomic percentage of nitrogen of 2.64 at% in the interfacial layer. This nitrogen content in the near interface region may help to passivate the Si dangling bonds, which may thus enhance the interface quality of oxide-semiconductor. The reported chemical properties of the film in this study may serve a key role in understanding their functional properties and lead to their application as advanced high- κ dielectric in MOS-based devices.

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