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Chemical Structure of SiN Films Deposited on High Aspect Trench by Plasma Enhanced Atomic Layer Deposition

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Abstract

We evaluated the chemical structures of the SiN films formed by ALD on the high aspect ratio trench substrates. Although the films were conformally deposited along the trench with uniform thickness, the chemical bonding states differs along the deep trench side wall showing different chemical shift revealed by angle-resolved hard X-ray photoelectron spectroscopy. The SiN bonding states exhibited chemical shift from stoichiometry to non-stoichiometry with increase the dept from the trench opening. The loss of the plasma activation for the N precursor might cause the insufficient reaction in the deep trench side wall.

1. Introduction

As a packing density in the large-scale integrated-circuit (LSI) becomes higher, the devices become consisted of three-dimensional complicated structure. The deep trench with high aspect ratio (AR), is one of the components to realize the structure [1]. The atomic layer deposition (ALD) is a technique suitable for such a trench structure, because which can conformally deposit a thin film along the high AR trench structure [2,3]. The ALD film theoretically consist of the same composition with the same thickness along the trench even for the high AR trench. In this study, we evaluated the ALD deposited SiN films along the deep trench with high AR of 3 and 7.5.

2. Experiment

10 nm-thick SiN films were deposited using alternate supply of SiH_2Cl_2 and plasma enhanced NH_3 precursor on the plane and trench structure with 40 nm opening and 120 or 300 nm deep, *i.e.* AR of 3 and 7.5, respectively at 350 and 550ºC. The fabricated samples were evaluated using, conventional X-ray photoelectron spectroscopy with AlKα X-ray source whose energy is 1486.6 eV (XPS), hard X-ray photoelectron spectroscopy (HAXPES), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and Fourier transform infrared spectroscopy (FT-IR). For the HAXPES evaluation, we carried out angle-resolved spectroscopy. Laboratory ready HAXPES (Lab. HAXPES) equipment, provided by Scient Omicron Inc., was used [4]. The X-ray source energy was 9251.74 eV form liquid GaKα. The photoemission angle (Take-off angle: TOA) was varied from 90 to 30 degree. Table I summarizes the samples used in this study [5].

Table. I Samples used in this study

Sample		Trench	SiN (nm)	Open (nm)	Depth (nm)	Temp (ºC)
A	Flat	-	10	-	-	350
	AR3	✓		40	150	
	AR7.5	✓		40	300	
B	Flat	-		-	-	550
	AR7.5	✓		40	300	

Figure 1 illustrates the trench sample schematics with the explanation of the angle-resolved HAXPES measurements [6]. One can understand by reducing the TOA from 90 degree, the photoelectron from the lower part of the trench side walls cannot reach to the photoelectron energy analyzer, therefore the measurement becomes top layer sensitive. We estimated the evaluation distances from the top of the trench sidewall in each TOA conditions based on the geometrical calculation as illustrate in Fig. 1. The detection ranges of the side wall of the trench are 150, 70, 40 and 23 nm for TOA75, 60, 45 and 30, respectively. It should also be noted that the trench bottom is also detected at TOA 90 in addition to the top of the trench.

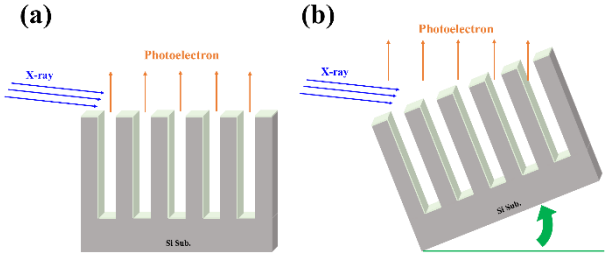

Fig. 1 Schematic of angle-resolved HAXPES of the trench sample with (a) TOA90, and (b) TOA60.

3. Results and Discussion

Figure 2 shows the cross-sectional TEM image for AR 7.5 deposited at 350°C with EDX mapping of N atoms. From Fig. 2 (a), we observed a uniform contrast along the trench. In addition, nitrogen is also incorporated along the trench as shown in Fig. 2(b).

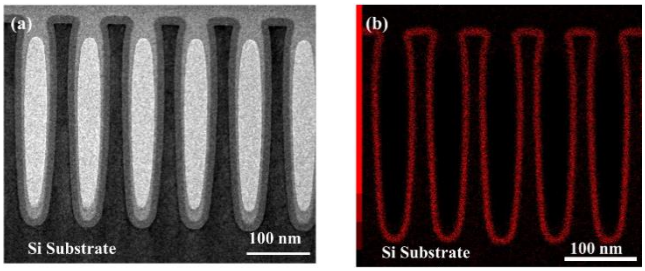

Fig. 2 Sample for AR 7.5 deposited at 350°C (a) cross-section TEM image, and (b) nitrogen EDX mapping.

However, the chemical structure might be different along the trench. Figure 3 shows the Si 1s spectra from the samples deposited at 350°C on the flat, AR 3 and 7.5 samples. The film on the flat surface, without trenches, showed mostly composed of Si-N (Si_3N_4) chemical bonds, while the spectra from the trench sample showed chemical shift on Si-N bonding states from stoichiometric to non-stoichiometric state. Moreover, the presence of the Si-O (SiO_x, $x < 2$) bonds were confirmed in the AR 3 and 7.5 samples in comparison with the flat sample [7,8]. From the above, the films on or in the trenches seem to be different from the flat surface.

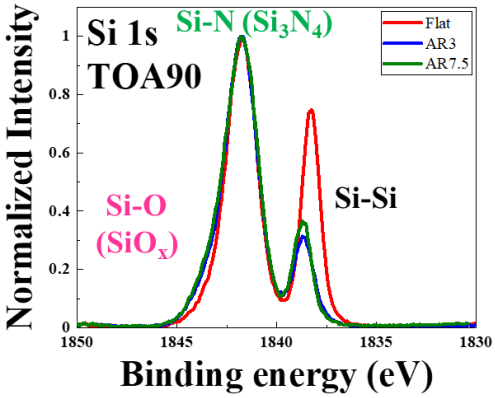

Fig. 3 Si 1s spectra with and without trench.

Figure 4 shows the angle-resolved HAXPES results for the trench samples AR3 and 7.5 deposited at 350°C. From Fig. 4 (a), it can be recognized that the Si-N bond in the Si spectra shifts from stoichiometry to non-stoichiometry on the lower energy side as the TOA decreases. Additionally, the Si-O component in the film decreased by reducing the TOA from 90 to 60, implying there are more oxide in the lower part of the trench than the upper part. The chemical shift in the Si-N bond changed from 1841.7 eV to 1841.4 eV. The AR3 measurement results shown in Fig .4 (b) also indicated the same tendency as AR7.5, although the Si-N peak shift was slightly smaller.

These peak shifts are affected by the difference in the detection depth, that is, the information on the trench side wall becomes dominant. We consider the plasma activated N precursors might lose their energy (activity) during the proceeding narrow high AR trench, resulting in the insufficient bonding with Si remained close to the bottom part of trench, which might be oxidized after the film deposition, although the film thickness seems to be the same for all over the trench structures. The stoichiometry uniformity was achieved by elevating the deposition temperature up to 550°C.

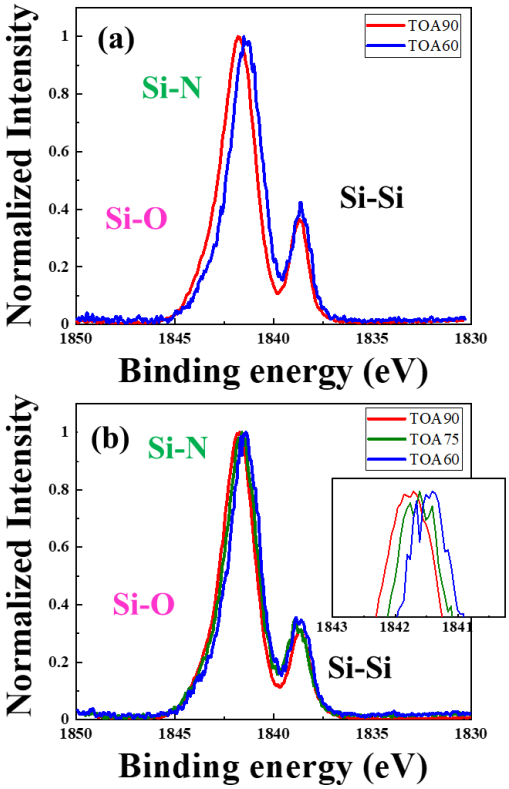

Fig. 4 TOA dependence of Si 1s spectra of AR7.5 fabricated at 350°C.

4. Conclusions

We have evaluated the plasma ALD SiN film conformally formed physically in the high AR trench and found that there are possible non-uniformity in the chemical along the deep trench. In particular, nitrogen deficiency begins to increase above 70 nm from the trench top on the trench side wall, resulting in the oxygen incorporation in the film.

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