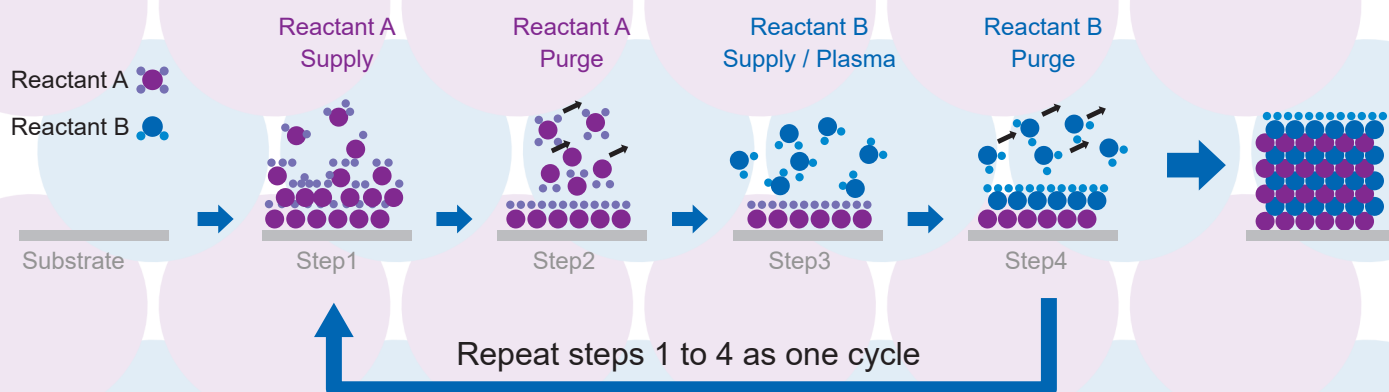


HfO₂ & ZrO₂ Film

Deposition by ALD

Samco Inc. Technical Report vol.115 / October 2021



1 H Hydrogen 1.01																	2 He Helium 4.00				
3 Li Lithium 6.94	4 Be Beryllium 9.01															5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31															13 Al Aluminum 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.07	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.39	31 Ga Gallium 69.72	32 Ge Germanium 72.61	33 As Arsenic 74.92	34 Se Selenium 78.96	35 Br Bromine 79.90	36 Kr Krypton 83.80				
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29				
55 Cs Cesium 132.91	56 Ba Barium 137.33	57 La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)				
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (269)	109 Mt Meitnerium (268)													

Introduction

HfO₂ and ZrO₂ are often applied as gate insulating films because of their higher dielectric constant compared to AlO_x and SiO₂. In addition, they show excellent chemical resistance and are used as a protective film against chemicals. HfO₂ and AlO_x multi-layer are also used as a water vapor barrier layer. Recent researches reported that HfO₂ films and mixed HfO₂ – ZrO₂ films of approximately 10 nm show ferroelectric properties, which is attracting attention for further research. Atomic Layer Deposition (ALD) enables excellent film thickness controllability and pinhole-free deposition and is suitable for deposition of ultra-thin films for gate insulators of FETs. In this report, we introduce the deposition of ALD-HfO₂ and ALD-ZrO₂ by the Samco thermal ALD system model “AL-1”.

Film Thickness Controllability

HfO₂ and ZrO₂ films were deposited on a Si substrate using TEMA₄Hf (Tetrakis (ethylmethylamino) hafnium), TEMA₄Zr (Tetrakis (ethylmethylamino) zirconium) and H₂O. The film thickness was measured by an ellipsometer. Figure 1 shows the relationship between the number of cycles and the film thickness deposited at 250°C. The film thickness increased in proportion to the number of cycles with 0.08 to 0.10 nm / cycle. Therefore, the film thickness was well controlled on the order of nanometer or less.

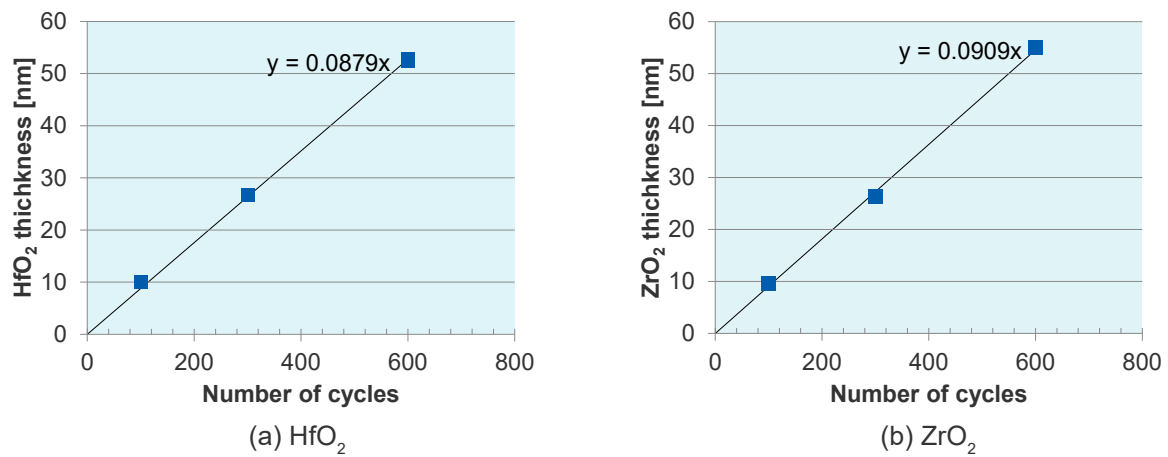


Figure 1. The number of cycles vs the film thickness of (a) HfO₂ and (b) ZrO₂

Additionally, the film uniformity was measured by placing Si chip samples on a ø230 mm carrier tray. The results are shown in the Figure 2. The thickness uniformity of the HfO₂ and the ZrO₂ film were $\pm 1.7\%$ and $\pm 3.8\%$ respectively when depositing the films of approximately 26.5 nm. The refractive index at $\lambda = 633$ nm is 2.077 to 2.093 for the HfO₂ film and 2.135 to 2.155 for the ZrO₂ film. The ZrO₂ shows a slightly higher refractive index than HfO₂.

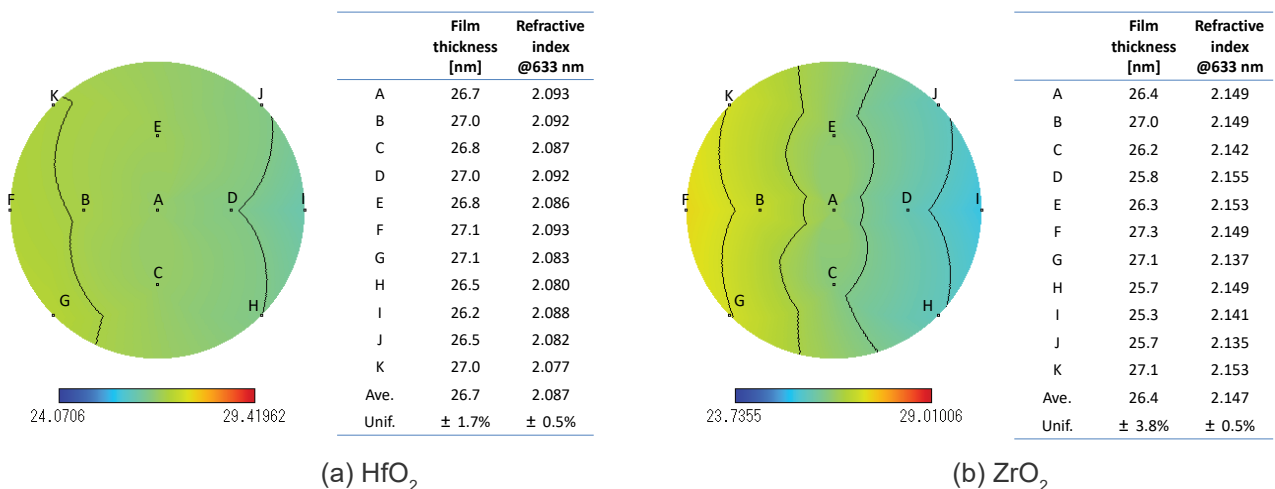


Figure 2. Film thickness and refractive index @ 633 nm uniformity of (a) HfO₂ and (b) ZrO₂

Step Coverage

The step coverage on a high aspect ratio structure is examined. The Si samples with trenches of an aspect ratio over 20 were prepared using Samco's Si DRIE system model: RIE-800iPB. The figure 3 shows the cross-sectional SEM images of the HfO_2 and ZrO_2 deposited at 250°C. Both HfO_2 and ZrO_2 were uniformly deposited from the top to the bottom of the trench pattern. In addition, the film traced the trench surface scallops fabricated by the Bosch process. These show the excellent step coverage – one of superior characteristics of ALD.

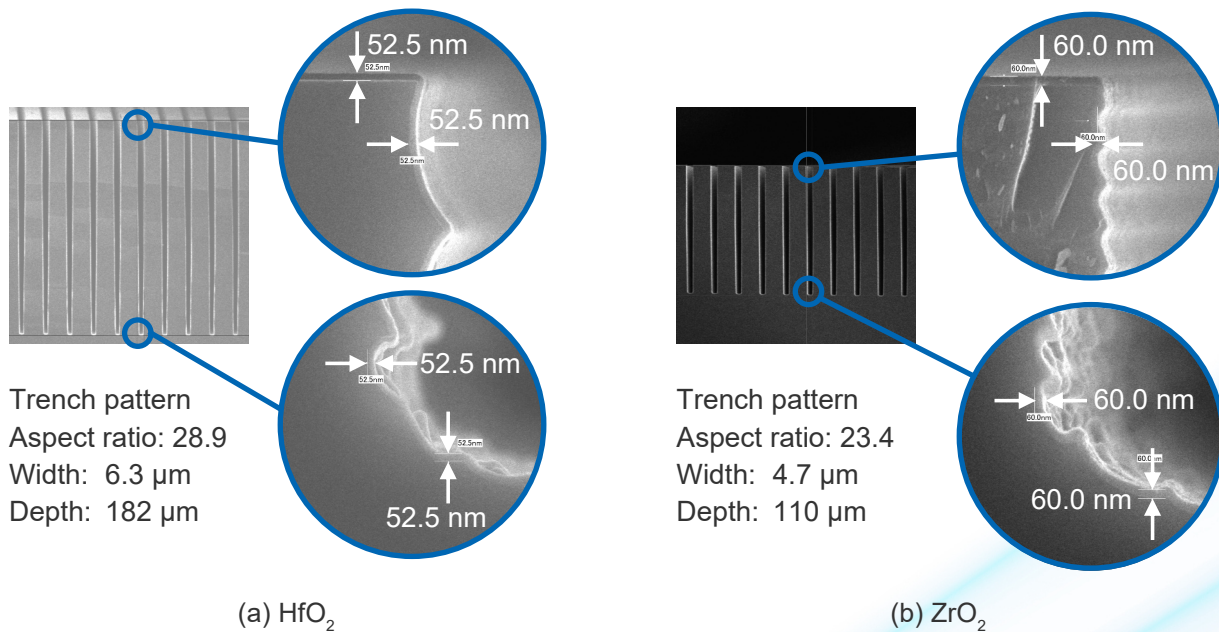


Figure 3. Cross-sectional SEM images of (a) HfO_2 and (b) ZrO_2 deposited on a high aspect ratio trench.

Conclusion

In this report, we introduced the HfO_2 and ZrO_2 deposition using the thermal ALD system model AL-1. The results show the excellent film thickness controllability and step coverage on the both films. We continue to evaluate performance of the ALD processes applied to a variety of devices and keep providing more solutions to realize customers' requirement.

Thermal ALD System AL-1



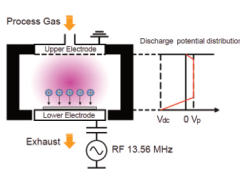
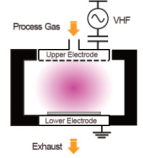
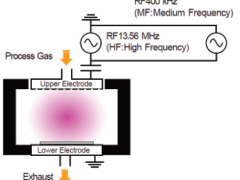
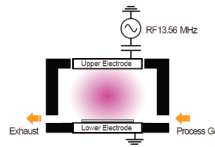
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From Kyoto to the forefront of semiconductor processing,
Samco's systems lead the way in Advanced Thin Film Technology

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We give teams reliable tools and resources, enabling your business or organization to push the limits of Thin Film Technology.

Four Pillars of Samco Deposition Systems

Cathode PECVD ■ 13.56 MHz is applied to the lower electrode to utilize the ion energy obtained from the sheath electric field on the cathode electrode ◆ Thick films can be deposited at high speed and low temperatures ◆ For SAW devices, optical waveguides, etc. 	VHF-PECVD ■ VHF bands such as 27, 40, and 60 MHz can be applied to the upper electrode to deposition with abundant radicals ◆ Low-damage deposition for RF devices ◆ For high-speed deposition of $\mu\text{c-Si}$ 
Dual-frequency PECVD ■ A wide process window is achieved by applying dual frequencies of 13.56 MHz and 400 kHz to the upper electrode. ◆ Excellent controllability of film stress ◆ For compound semiconductors, electronic devices 	PE & Thermal ALD ■ One atomic layer is deposited by repeating the supply of precursor and purging of excess precursor. ◆ Excellent step coverage ◆ For gate oxides for electronic devices 

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