Supplementary Information for:

Nanoporous SiCOH/C_xH_y dual phase films with an ultralow dielectric constant and a high Young's modulus

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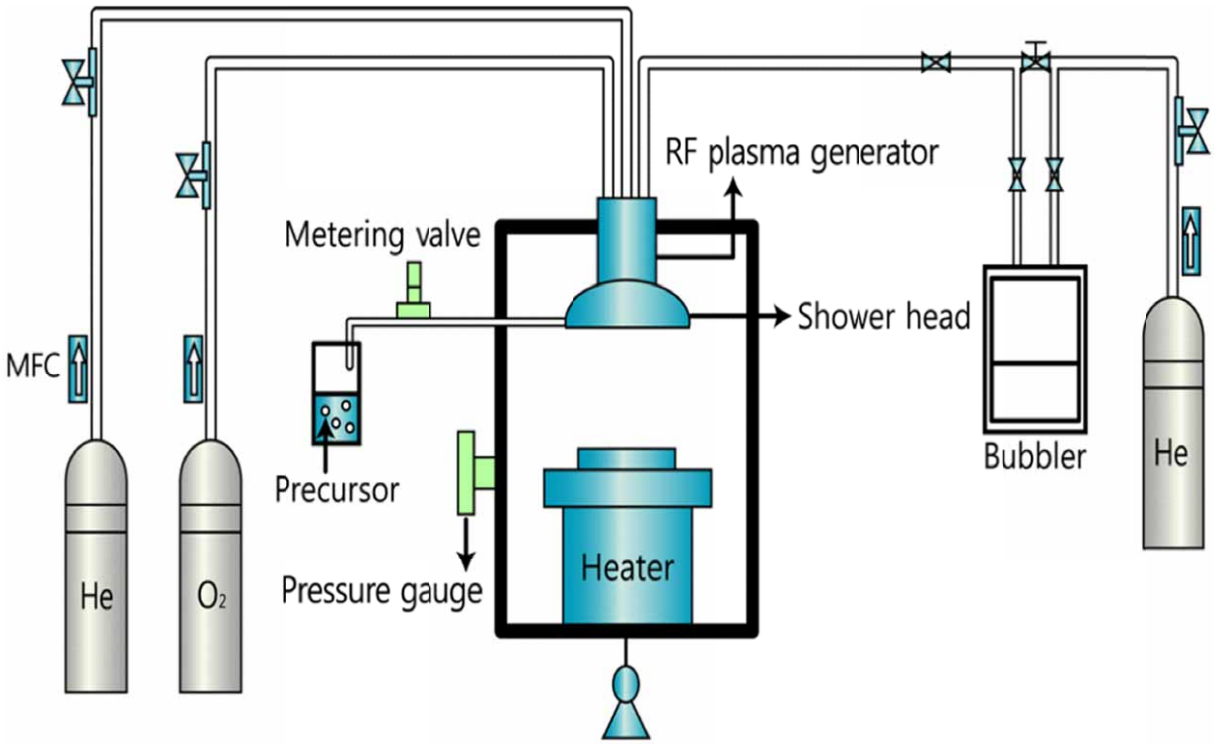

Scheme S1 A schematic representation of the PECVD reactor setup for coating on flat substrates.

We installed the PECVD reactor (Scheme S1) for coating two precursors. A plasma reactor was used to generate radical oxygen in between the shower head and the substrate. ATMS and CHO gases were mixed in the mainstream of the plasma, and flowed toward the substrate. The film was deposited on silicon substrates.

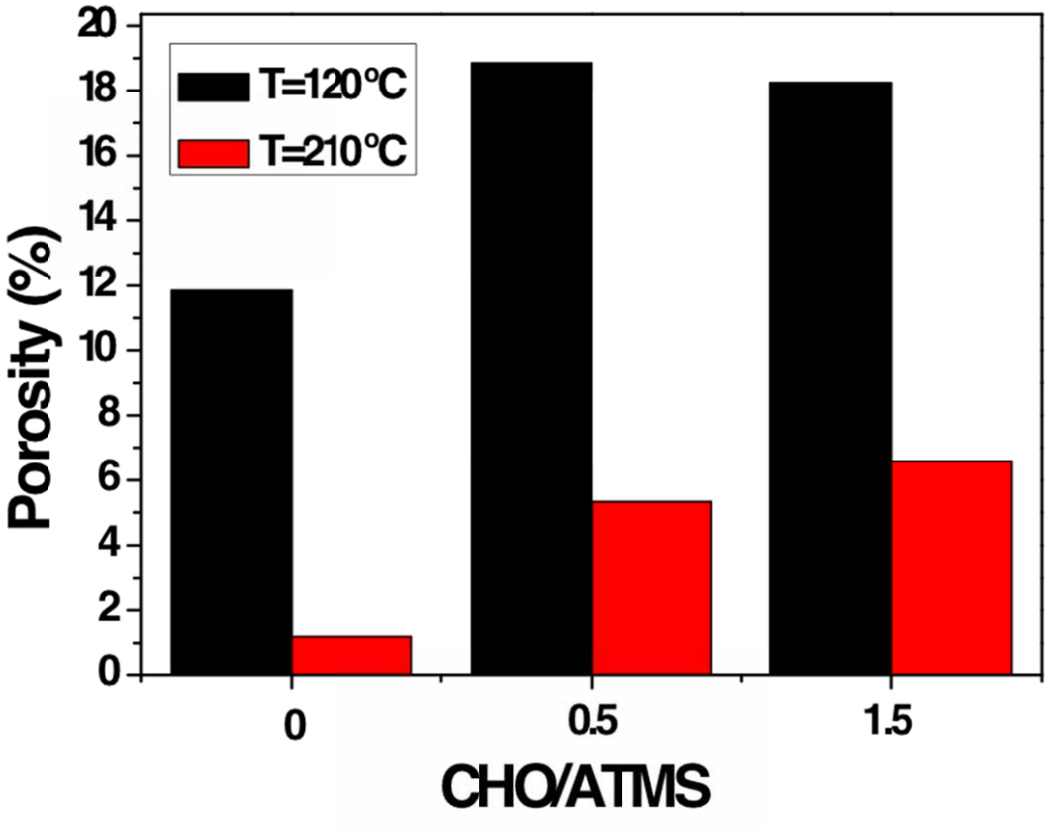

Fig. S1 Additional Porosity of the ATMS and ATMS/CHO dielectric films as a function of the CHO/ATMS ratio at each deposition temperature. The O_2/ATMS ratio was 2.5 and the films were annealed at 420 °C.

$$\text{The } Si - CH_3/Si - O \text{ peak ratio} =$$

$$[Si - CH_3\ (1250 - 1280\ cm^{-1})/Si - O\ (1000 - 1200\ cm^{-1})] \quad \text{(S1)}$$

$$\text{The } CH_m/Si - O \text{ peak ratio} =$$

$$[CH_m\ (2950 - 3000\ cm^{-1})/Si - O\ (1000 - 1200\ cm^{-1})] \quad \text{(S2)}$$

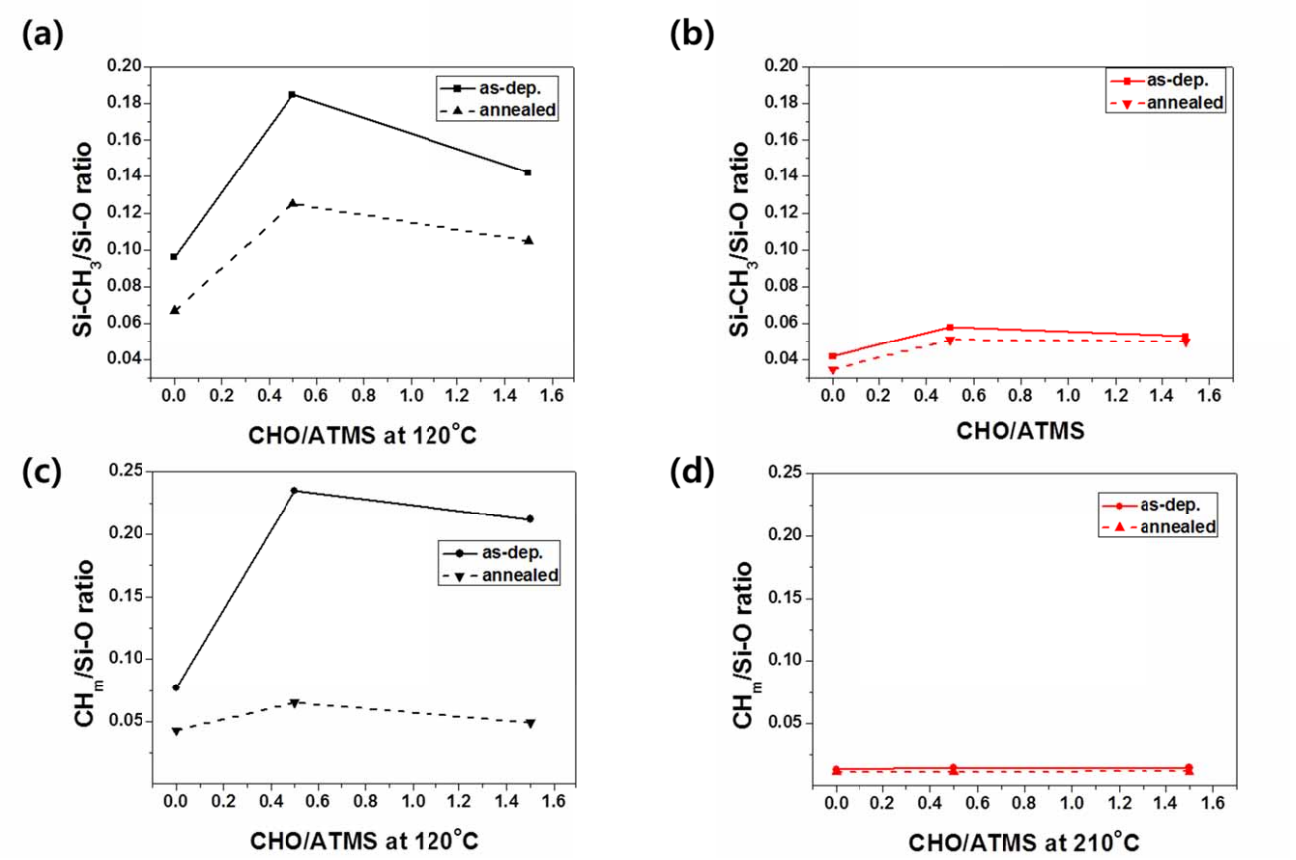

Fig. S2 The Si-CH_3/Si-O and CH_m/Si-O peak ratio in the ATMS and ATMS/CHO dielectric films as a function of the CHO/ATMS ratio at each deposition temperature. The O_2/ATMS ratio was 2.5 and the films were annealed at 420 °C.

For the films deposited at 120 °C, the range of the Si-CH_3/Si-O peak ratio was 0.10-0.18 in the as-deposited films, and the peak ratio was reduced to 0.06-0.12 after annealing at 420 °C in Ar atmosphere for 2 hr. The CH_m/Si-O peak ratio, 0.08-0.23, of the as-deposited films decreased to 0.04-0.06 after annealing as well. This trend is similar to the films deposited at 210 °C. It seems that both thermally labile groups (C_xH_y) and Si-CH_3 were removed after annealing at 420 °C. The Si-CH_3 content as well as the CH_m content decreased after annealing at 420 °C.[22, 34] The desorption of carbon groups such as CH_3 and CH_m can increase the porosity of the film and decrease the dielectric constant. The value of Si-CH_3/Si-O and CH_m/Si-O peak ratios for the deposition temperature of 120 °C are relatively higher than those for 210 °C. For this reason, it is estimated that the dielectric constant of the deposited films at 120 °C is lower than that of the films at 210 °C.

Table S1. The effect of substrate temperature and annealing on the amount of each chemical component in the ATMS/CHO dielectric film. The O_2/ATMS ratio was 2.5, the CHO/ATMS ratio was 0.5, and the dielectric films were annealed at 420 °C.

	Deposition Temp. = 120 °C		**Deposition Temp. = 210 °C**
	As-deposited [%]	**Annealed [%]**	**Annealed [%]**
SiO_0	10.69	5.06	1.04
SiO_1	38.73	18.83	6.07
SiO_2	38.58	43.08	**42.06**
SiO_3	12	31.37	**46.37**
SiO_4	0	1.67	**4.45**
Sub-total	100	100	100
$C(Si)_n$	29.7	30.04	21.99
$Si-CH_3$	55.49	50.7	**58.53**
CO_1	9.36	13.55	12.43
CO_2	5.45	5.71	7.05
Sub-total	100	100	100

Table S2. A comparison table between this study and previously reported dielectric constants and moduli of low-k SiCOH films.[18-22,62-64]

Dielectric constant	Modulus [GPa]	Ref.
2.6	6.4	Jousseaume et al., *J. Electrochem. Soc.*, 2007.
2.4	3.5	Burkey et al., *J. Electrochem. Soc.*, 2004.
2.4	9	Frot et al., *Adv. Funct. Mater.*, 2012.
2.4	**8.4**	**This work**
2.3	5.9	Rathore et al., *Adv. Funct. Mater.*, 2008.
2.3	4.1	Dubois et al., *Proc. IEEE Int. Interconnect Technol. Conf.*, 2005.
2.2	5.4	Trujillo et al., *Adv. Funct. Mater.*, 2010.
2.2	6~7	Eslava et al., *J. Am. Chem. Soc.*, 2008.
2.2	11	Eslava et al., *J. Am. Chem. Soc.*, 2007

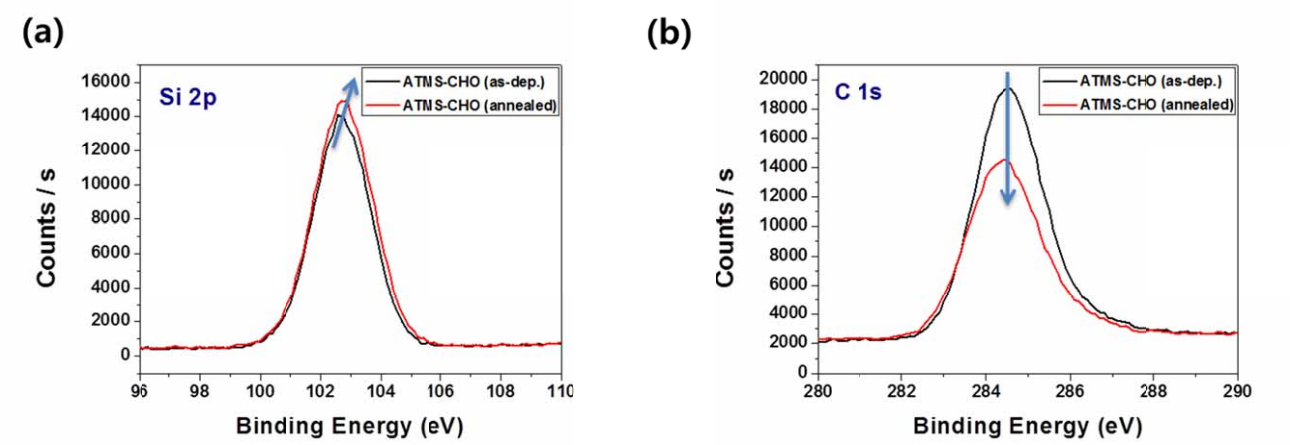

Fig. S3 XPS analysis of ATMS/CHO dielectric films deposited at 210 °C; (a) Si2p spectra and (b) C1s spectra. The peak shift and the intensity change after annealing at 420 °C are represented in (a) and (b).

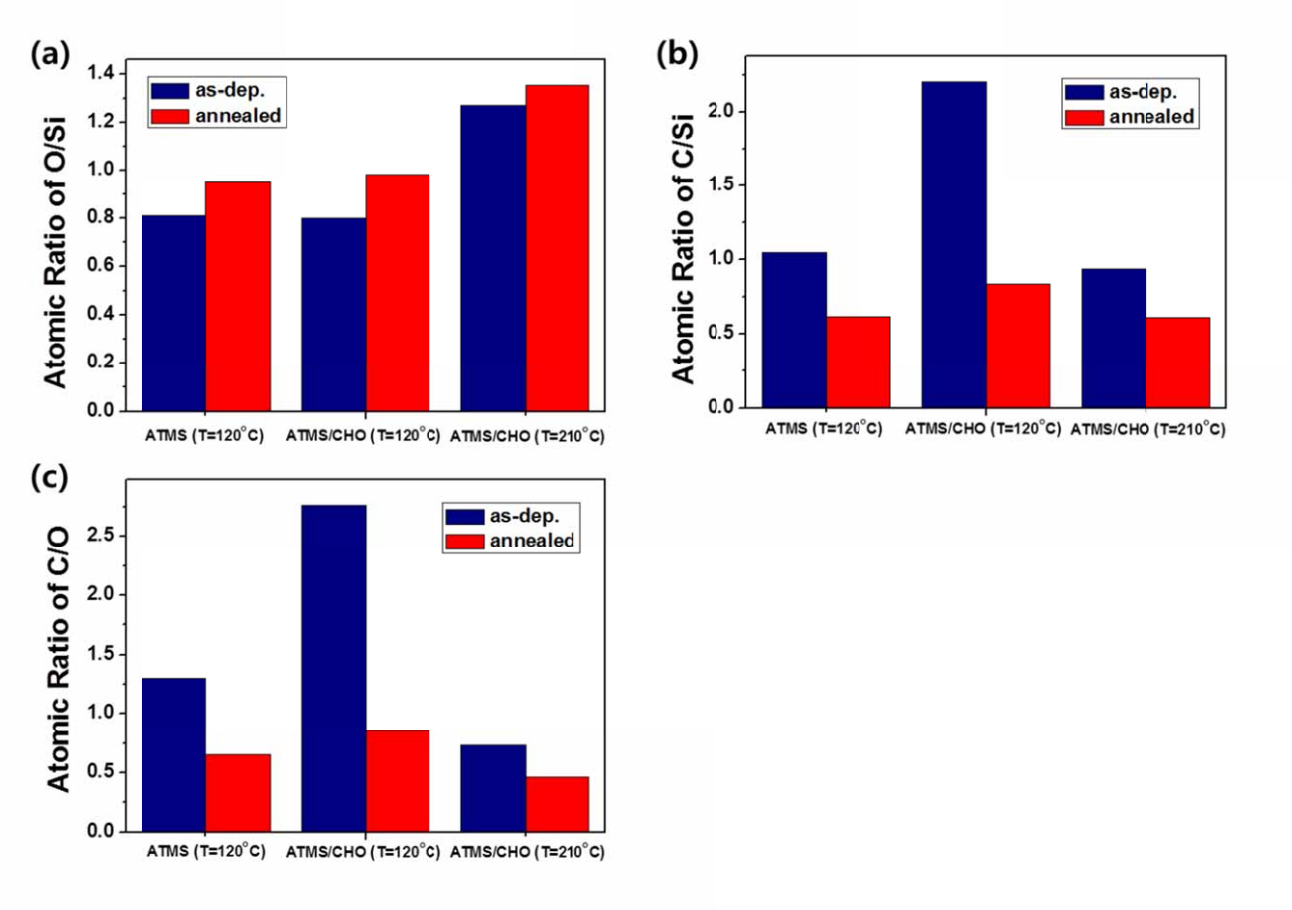

Fig. S4 The atomic ratio (a) O/Si, (b) C/Si and (c) C/O that were obtained from XPS charts of ATMS/CHO dielectric films as a function of the deposition temperature. The O2/ATMS ratio was 2.5 and dielectric films were annealed at 420 °C.

When we calculated the overall atomic ratio of O/Si, C/Si, and C/O based on the peak areas (Fig. S4), with the increase of the substrate temperature from 120 °C to 210 °C, the C/O and C/Si ratios were reduced from 0.86 and 0.84 to 0.46 and 0.61 after annealing, respectively. This is a similar result to that of V4D4 (tetravinyltetramethylcyclotetrasiloxane) low-k films.[22] In short, the higher the substrate temperature, the higher the oxygen content and the lower the carbon content. Therefore, the ATMS/CHO dielectric films deposited at 120 °C shows a higher carbon content, followed by a lower dielectric constant after annealing. The Si 2p peak was shifted from 101.7 eV to 102.6 eV after annealing (Fig. 4c, 4e, S2a). This indicates that Si-O moieties changed from SiO_0 and SiO_1 to SiO_3 and SiO_4.

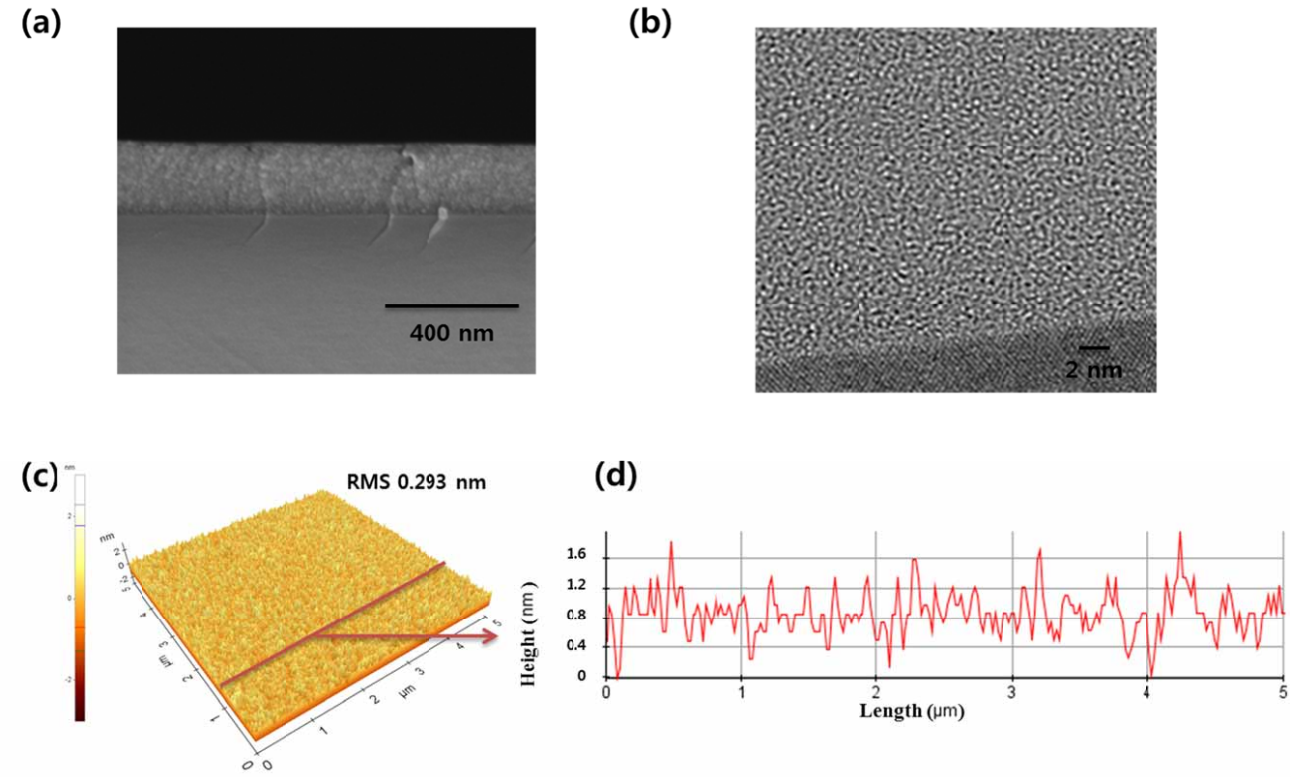

Fig. S5 Typical images of the ATMS/CHO dielectric film; (a) cross-sectional SEM image, (b) TEM image, (c) AFM image, and (d) cross-sectional AFM profile measured along the indicated plane.

Fig. S5 shows a typical FE-SEM cross-sectional image of the ATMS/CHO dielectric film. The film is amorphous in structure with a thickness of ~ 300 nm. It was observed in the TEM image of a typical amorphous structure in SiCOH films (Fig. S5b). The surface microstructure of the film was very smooth, uniform, and defect free in both the as-deposited and annealed samples. In the AFM image (Fig. S5c) and its corresponding height profile (Fig. S5d), the film shows a very low RMS (Root Mean Square) of 0.293 nm and small ridges with a maximum height of 1.8 nm.

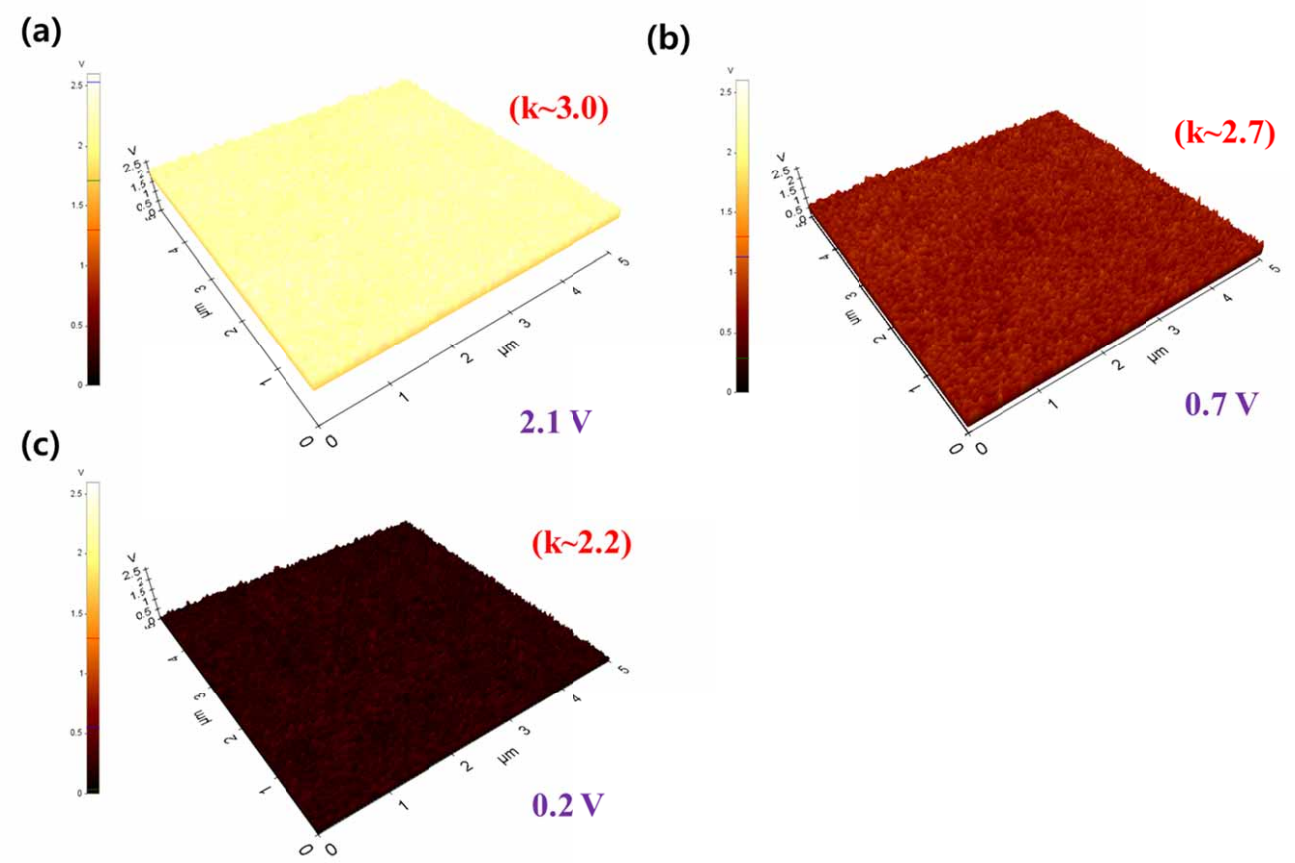

Fig. S6 EFM images of ATMS and ATMS/CHO dielectric films deposited at 120 °C as a function of precursor-selection and post-treatment. (a) ATMS (as-deposited), (b) ATMS (annealed), (c) ATMS/CHO (annealed). The O_2/ATMS ratio was 2.5 and the annealing temperature was 420 °C.

We measured the dielectric constants of the dielectric materials using electrostatic force microscope (EFM) analysis, which is easier than the capacitance-voltage (C-V) measurement of the metal/insulator /semiconductor (MIS) structure (Fig. S6). An additional benefit of EFM is that it can check the uniformity of the dielectric constant in the films. The dielectric property of the films is related to the capacitance, which is evaluated from the surface charge. The surface charge is found from the difference of the electric potential or the electrostatic capacitance.[1–3] The scan rate was fixed at 1 Hz using oscillation and non-contact mode. A bias voltage (7 V) between the tip and the sample was applied by an external battery, forming a capacitor. From EFM results of ATMS and ATMS/CHO composite films, we found that the distribution of the electric potentials on the surface in ATMS (as-deposited), ATMS (annealed), and ATMS/CHO (annealed) films were very uniform, and that those of the films were 2.1 V, 0.7 V, and 0.2 V, respectively. Therefore, the dielectric constant of ATMS/CHO (annealed) films was lower than that of ATMS alone.

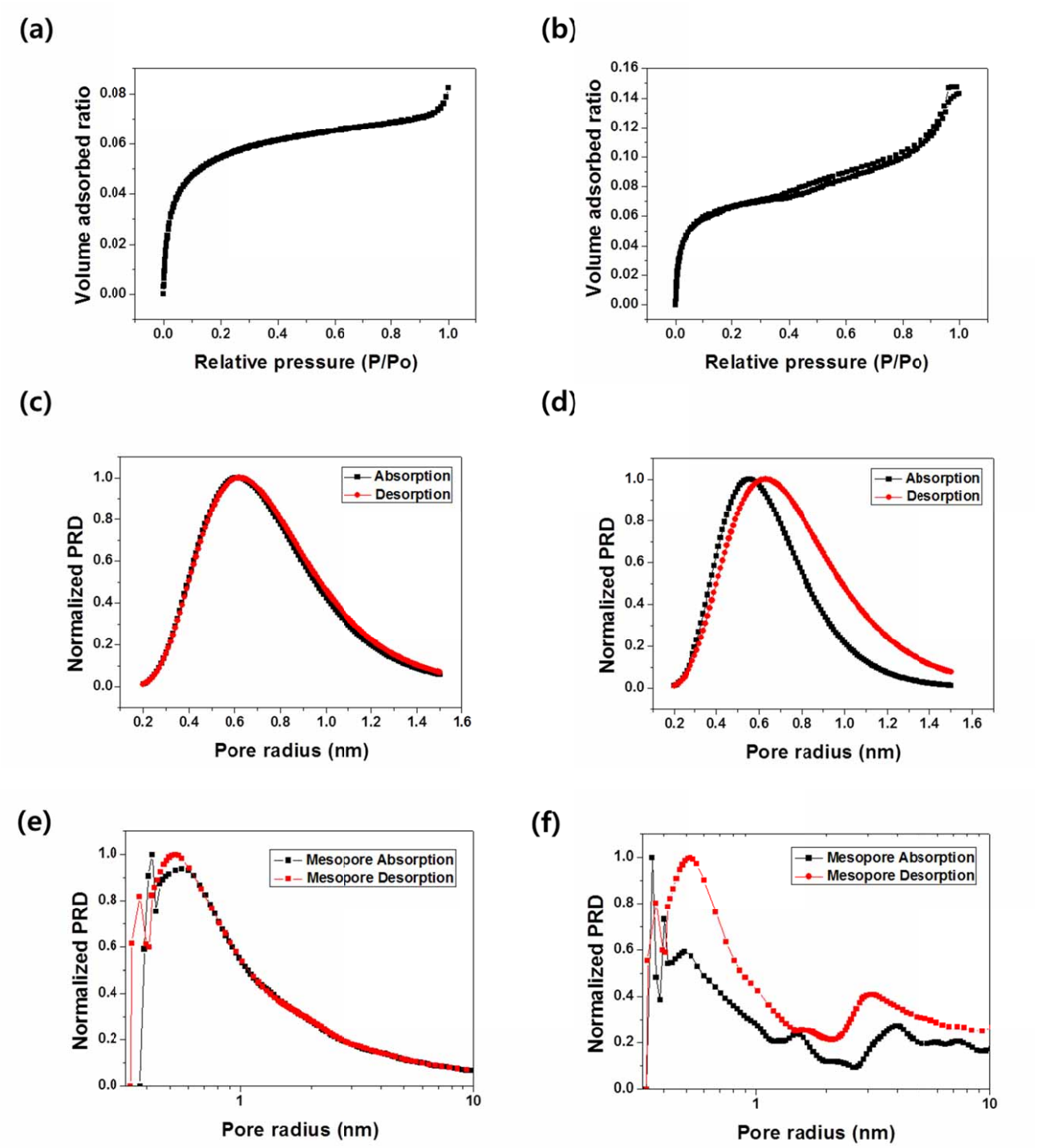

Fig. S7 Toluene adsorption-desorption isotherm plots (a, b) and pore size distributions (c-f) of ATMS and ATMS/CHO dielectric films deposited at 210 °C as a function of precursor-selection. (a, c) ATMS only (b, d) ATMS/CHO dielectric films. The O_2/ATMS ratio was 2.5 and the annealing temperature was 420 °C.

The standard measurement protocol is as follows: Samples was heated up to 150 °C for 5 min before porosimetry measurement on a separate hot plate. Wafers was placed in vacuum chamber, then porosimetry cycle with toluene as solvent chemical. Spectroscopic ellipsometric porosimetry measurements was evaluated automatically. Samples were located in an adaptation plate on the robot loader arm of the PS-2000 ellipsometric porosimeter system.

The porosity and average pore radius of ATMS only films were 7.4 % and 0.61 nm, respectively. Those of ATMS/CHO dielectric films were 14 % and 0.58 nm using EP data (Fig. S7). Pore Radius Distribution (PRD) were desirably narrow and microporous below 1.6 nm (Fig. S7 c, d). In ATMS only and ATMS/CHO system, the main pore size was about 0.5~0.6 nm, of which the main portion was microporous rather than mesoporous. Also, the region of mesoporus part in ATMS/CHO system was relatively higher than ATMS only films. EP measures the change of the optical properties and thickness of the materials during an adsorption experiment. During the experiment, the pores in the layer are filled gradually by adsorptive (solvent) material such as toluene. Change of optical properties, detected by spectroscopic ellipsometry (an optical technique). Pore analysis is considered Dubinin-Radushkevich (DR) model and modified Kelvin equation. Pore size distribution (PSD) calculated from refractive index/volume adsorbed isotherm. First, the volume adsorbed isotherm is calculated from the refractive index isotherm (Lorentz-Lorenz equation).[4]

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[3] D. M. Chiang, W. L. Liu, J. L. Chen and R. Susuki, *Chem. Phys. Lett.*, 2005, **412**, 50.

[4] F. Rouquerol, J. Rouquerol and K. S. W. Sing, *Adsorption by Powders and Porous Solids*, Academic Press Inc., 1999.