Supplementary Information for JACS Communication

"nm- thick Conformal Pore-sealing of Self-assembled Mesoporous Silica by Plasma-assisted Atomic Layer Deposition"

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I. Behavior of regular thermal ALD on an uncapped mesoporous substrate

We have found that for a mesoporous low-k silica film without a capping layer, regular thermal ALD will penetrate into the internal porosity, filling its pores and increasing its effective "k" value. At optimized conditions, this ALD deposition is a conformal coating on the surface of nanopores (Fig. S1). On the other hand, this also indicates that ALD can precisely reduce the pore size and modify the pore surface chemistry of mesoporous materials. With the assistance of plasma, the location of this pore size reduction and surface modification can be defined to the immediate surface of a mesoporous material.

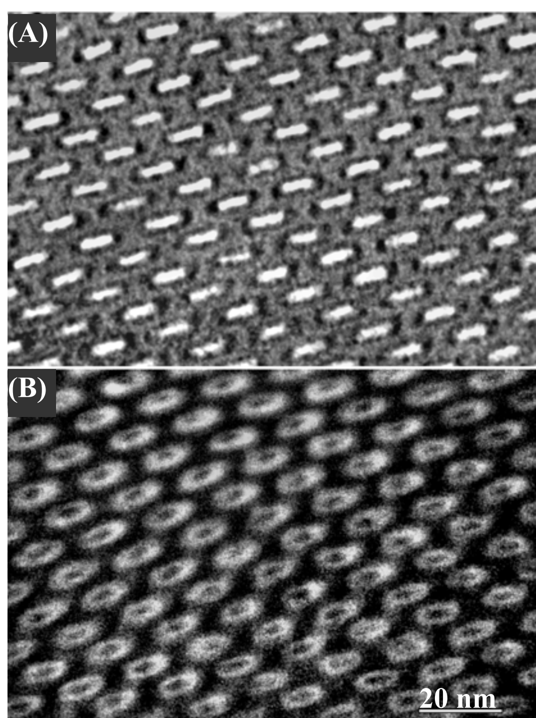


Figure S1. Cross-sectional TEM images of uncapped self-assembled mesoporous silica after TiO_2 ALD using $TiCl_4$ and H_2O as precursors: (A) TEM image acquired with regular operations. The dark edges on the voids are the TiO_2 ALD layers; (B) the corresponding Ti-map acquired with Gatan Image Filter for the same area. The bright regions identify the TiO_2 location.

II. The idea of using remote plasma to define the location of ALD

In our work, the purpose of the plasma is to define the location of ALD. If ALD precursors are chosen to be non-reactive unless triggered by plasma, then, the location of ALD is defined by that of the plasma irradiation.

The Debye length of a typical plasma is on the scale of micrometers. On the other hand, the particle mean free path in a typical plasma usually varies from several microns to tens millimeters. Both are much larger than the pore dimension of a nanoporous low-*k* material (Angstoms to several nm). For this reason, a typical plasma cannot penetrate within the internal porosity of a low-k material, confining PA-ALD to the immediate surface of a nanoporous material (Fig. S2a).

Here we emphasize the use of a remote plasma. An intensive plasma may cause significant heating (resulting in a type of thermal ALD mechanism) and ion bombardment damage to the sample surface. In our experiments, we performed numerous preliminary experiments to map out the plasma intensity and to locate a remote plasma zone where the ion bombardment is reduced while the active particles are still plentiful: the saturation ion current to the sample surface was measured to seek the conditions for reduced ion bombardment (Fig. S2b), and the carbon etch rate by the same oxygen- plasma was monitored to ensure enough active radicals for ALD reaction.

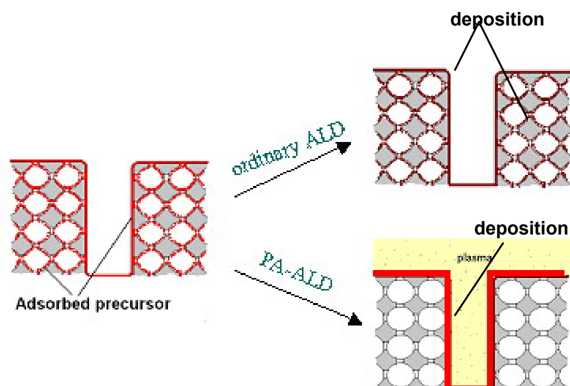
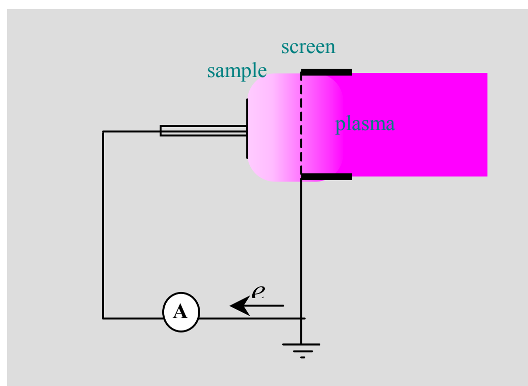


Figure S2a Schematic illustrating the comparison between ordinary ALD and PA-ALD. In PA-ALD, since plasma cannot penetrate within the internal porosity of a low-k material due to the fact that the pore dimensions of nanoporous low-*k* materials are much smaller than the Debye length (on the order of μm scale) and the particle mean free path (ranging from μm to mm) in a typical plasma, ALD is confined to the immediate surface of these nanoporous materials



$$I_i^{sat} = n_i e S(kT_e/2\delta m_i)^{1/2}$$

Figure S2b Schematic illustrating saturation ion current measurement to sample surface. A screen was used in front of the sample stage. This configuration resembles an asymmetric Langmuir probe. The gradient plasma between sample and screen leads to an intrinsic electron stream flowing from the screen to the sample via external circuit, and the maximum current of this stream is limited by the amount of ions available in the sample vicinity to neutralize the electrons (in other words, limited by the saturation ion current to the sample surface). Therefore, from this intrinsic current, the ion density in the sample vicinity or the intensity of ion bombardment can be estimated.

III. The impact of PA-ALD on dielectric constant of mesoporous low-k silica

Our measurements suggest that there is no pronounced impact of the PA-ALD process on the dielectric constants of the mesoporous low-k silica films. Table S1 shows the comparison of dielectric constants before and after PA-ALD.

Table S1 Comparison of k before and after PA-ALD

	Original mesoporous silica	**After PA-ALD**
Film thickness	205 nm	210 nm
Capacitance:	0.512 nF (average of 9 measurements)	0.526 nF (average of 9 measurements)
Area of electrode:	4.91 mm^2	4.91 mm^2
“k” thus measured:	**2.42**	**2.49**

Procedure of k measurements:

1. To make the conductive substrates, a 20nmTi/300nmAu/20nmTi multi-layer was coated on a Si wafer by e-beam evaporation.
2. Brij-56 mesoporous silica was coated on those substrates and 10% of the TEOS precursor was replaced by MTES ($CH_3Si(OEt)_3$) to introduce -CH_3 on the pore surface. The surfactant was removed by extraction after baking at 120 ^oC for 48 hrs.
3. Mesoporous silica was further heat-treated at 250 ^oC in Ar+2%H_2 for 4 hrs. Then the mesoporous silica was further dehydroxylated at 180 ^oC with TMCS ($(CH_3)_3SiCl$) vapor in a vacuum tube.
4. The mesoporous silica sample was split into two pieces. One was capped by PA-ALD SiO_2 and the other remained untouched.
5. Both pieces were evaporated with 20nmTi/300nmAl to form the top electrodes for capacitors. A mask with 2.5 mm holes was used to define the area of these electrodes (Fig. S3).
6. Capacitances were measured with a 1 MHz AC signal generator and RC bridge.
7. “k” values were calculated with equation $k=(d*C)/(\varepsilon*A)$, where:
   k – dielectric constant
   d – mesoporous silica film thickness
   C – capacitance
   ε – vacuum dielectric permittivity: $8.854x10^{-12}$ F/m
   A –area of the capacitor plates

Figure S3 Picture of capacitors for “k” measurements formed with mesoporous silica film on Au-coated Si substrate and 2.5 mm Al electrodes on top