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A new procedure to seal the pores of mesoporous low-k films with precondensed organosilica oligomers

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Preparation of mesoporous silica film.

0.3 g Brij-76 was dissolved in 20 ml ethanol and 0.5 ml (0.1M) HCl. Then, 1 ml of Tetraethyl orthosilicate (TEOS) and 0.5 ml H_2O were added to the solution and this was aged for 1 day. The solution was then spin-coated on a Si-wafer at a rate of 5000 rpm. The porogen was removed by treating the film at 400 °C for 5 h.

Preparation of mesoporous ethylene-bridged organosilica film.

1.2 g Brij-76 was dissolved in 20 ml ethanol and 1.5 ml (0.1M) HCl. Then, 3 ml of 1,2-bis(triethoxysilyl)ethane and 1.5 ml H_2O were added to the solution and this was aged for 1 day. The solution was then spin-coated on a Si-wafer at a rate of 5000 rpm. The porogen was removed by treating the film at 400 °C for 5 h.

Preparation of the cyclic carbon-bridged organosilanes.[1,2]

A solution of 70 ml 0.5 w% $FeCl_3$ in dry THF was added to 7 g Mg turnings and stirred until a grey colored mixture was visible. This mixture was kept under an inert atmosphere. Then, a solution of 100 ml 14.2 v% chloromethyl triethoxysilane in dry THF was rapidly added to the mixture and stirred for 48 h at 50 °C. The mixture was filtered off and the solvent was removed from the filtrate. Pentane was added to the residue and this mixture was also filtered. The remaining oil consists of cyclic carbon-bridged organosilanes.

Preparation of the organosilica dense layer.

0.5 ml of the cyclic carbon-bridged organosilane mixture was dissolved in 20 ml ethanol, 0.5 ml (0.1M) HCl and 0.5 ml H_2O and aged for 1 week. The solution was then spin-coated at 5000 rpm on top of the mesoporous silica film to form an organosilica top layer. An additional baking step was performed at 400 °C under nitrogen atmosphere to remove all the volatiles and to complete the condensation of the cyclic carbon-bridged precursor.

HMDS treatment

The vacuum dried film was exposed to HMDS vapor for 2 h at 130 °C and rinsed with pentane to remove unreacted HMDS.

Characterization methods

Ellipsometry

The refractive index and thickness of the layer is analyzed on a J. A. Woollam ellispometer alpha-SE. This non destructive method measures the change in polarization of the reflected light off a sample. By using a mathematical model, the thickness and refractive index are calculated. Having knowledge of the refractive index, it is now possible to calculate the theoretical porosity by using the Lorentz-Lorenz equation (1).

$$\frac{n^2-1}{n^2+2} = V_p \frac{n_p^2-1}{n_p^2+2} + (1-V_p)\frac{n_s^2-1}{n_s^2+2} \quad (1)$$

In this formula, n_p stands for the refractive index of the material inside the pores (in our case air with $n_p = 1$).The refractive index of the material containing the pores n_s (in our case SiO_2 with $n_s = 1.46$). By measuring n by ellipsometry, we can now easily calculate the porosity V_p.

For the determination of the porosity and pore radius distribution, a spectroscopic ellipsometer Sentech 801 at 70° incidence angle is mounted in a vacuum chamber that can be filled with solvent vapor (toluene) in a controlled way. The pressure of the toluene vapor is raised in steps from the vacuum level up to the saturation pressure. The pressure dependent condensation occurs in the open pores and the refractive index of the sample is changed. The total pore volume is calculated from the change in refractive index using following equation.

$$P = \left(\frac{n_{rf}^2-1}{n_{rf}^2+2} - \frac{n_{re}^2-1}{n_{re}^2+2}\right) / \left(\frac{n_{ads}^2-1}{n_{ads}^2+2}\right) \quad (2)$$

With P the porosity, n_{re} the refractive index of the film with empty pores, n_{rf} the refractive index of the film with filled pores and n_{ads} the refractive index of the solvent. The pore radius is calculated from the adsorption branch with the Kelvin equation taking into account the physical properties of toluene.

$$\ln\frac{P}{P_0} = \frac{-2\gamma V}{rRT} \quad (3)$$

With P/P_0 the relative pressure, γ the surface tension of toluene, V the molar volume of toluene, r the pore radius, R the gas constant and T the temperature.

Water contact angle values were obtained by using a Krüss-DSA 30 Drop Shape Analysis System using the tangent 1 model.

Diffuse reflectance fourier transform infra-red (DRIFT) spectra were obtained on a Nicolet 6700 FT-IR from Thermo Scientific.

The dielectric constant of the films was calculated from the capacitance of a parallel plate capacitor at 100 kHz using a HP 4192A LF impedance analyzer. Aluminium dots were used as top contact and a heavily doped silicon wafer was used as bottom contact. The bottom of the silicon wafer was scratched to remove the native silicon dioxide and an eutectic indium/gallium alloy was attached to make a good ohmic contact with the impedance analyzer.

Water adsorption isotherm

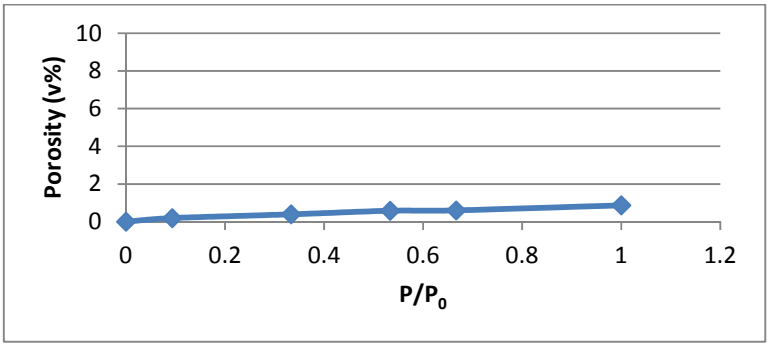

Figure S1: Water adsorption isotherm of the ethylene-bridged organosilica film after sealing.

References

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