Ellipsometry Porosimetry for Ultra Low K Material

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UCLA July 2006
Excellent dielectric properties of SiO₂ have been the cornerstone for microelectronic revolution during the past 30 years.

Technology challenge: reduce RC delay

$$RC = 2 \rho k \varepsilon_0 \left( \frac{4L^2}{P^2} + \frac{L^2}{T^2} \right)$$

ρ - metal resistivity
k - relative dielectric constant
L - line length
P - metal pitch
T - metal/dielectric thickness

Better Interconnects require:
1. Metals with low resistivity (Cu)
2. Dielectrics with low dielectric constant (low-k)

Introduction of porous low K materials
• EP is a unique technology to characterize CVD and spin coated porous ultra low K.

• EP measures the change of the optical properties and thickness of the materials during adsorption and desorption of an organic solvent.

• The analysis gives:
  • porosity of the Low K
  • pore size distribution
  • Average pore size
  • For both microporous and mesoporous, cumulative surface area, pore interconnectivity, Young modulus, thickness and refractive index.

• EP qualifies the sealing layer of both patterned and blanket wafers.

Adrien Darragon - Product Manager, SOPRA – sales@sopra-sa.com
1. Principle and measurement setup
2. Porosity and Pore size measurements
   • Mesoporous
   • Microporous
3. Young modulus
4. Pore killers and sealing
   • Blanket wafers
   • Patterned wafers
   • Interconnectivity
Porosity measurement

From the thickness and refractive index measurements on the basis of Lorentz-Lorenz equation:

From adsorption/desorption isotherms:
- Porosity
- Pore interconnectivity

No need to know the dense skeleton material properties
ELLIPSOMETRY is a method based on measurement of the change of the polarisation state of light after reflection at non normal incidence on the surface to study.

\[ E_{\text{out}} = r \ E_{\text{in}} = (\tan \gamma \ e^{i \Delta}) \ E_{\text{in}} \]

Ellipsometry measures \( \tan \gamma \) and \( \cos \Delta \).
Physical parameters $n, k$ Thickness

Experimental Measurement

- $\tan Y$
- $\cos D$

Physical Model

With an estimated sample structure

- Film Stack and structure
- Material $n$, $k$, dispersion
- Composition Fraction of Mixture

Calculated values

- $\tan Y$
- $\cos D$

Advanced minimization algorithms
for quick convergence

Experimental Measurement = Model Simulation?

No, proposition for new parameters

Yes

Film structure and optical properties proposed are correct.
Porosity measurement

**Lorentz-Lorenz equations**

**Dense prototype:**

\[ B_1 = \frac{n_{rd}^2 - 1}{n_{rd}^2 + 2} = \frac{n_2^2 - 1}{n_2^2 + 2} \]

**Empty pores:**

\[ B_2 = \frac{n_{re}^2 - 1}{n_{re}^2 + 2} = V \left( \frac{n_1^2 - 1}{n_1^2 + 2} + (1-V) \frac{n_2^2 - 1}{n_2^2 + 2} \right) = (1-V) \frac{n_2^2 - 1}{n_2^2 + 2} \]

**Liquid in pores:**

\[ B_3 = \frac{n_{rl}^2 - 1}{n_{rl}^2 + 2} = V \left( \frac{n_{ads}^2 - 1}{n_{ads}^2 + 2} + (1-V) \frac{n_2^2 - 1}{n_2^2 + 2} \right) \]

- The skeleton refractive index \( n_2 \) defines the measured refractive index \( n_r \) and Volume Polarisability \( B_1 \).
- \( n_{re} = 1 \) and Volume Polarisability \( (B_2) \) depends on \( n_2 \) and porosity.
- Pores filled by liquid: Volume Polarisability \( (B_3) \) depends on \( n_2, n_{ads} \) and porosity.

\( n_{re} \): refractive index measured when pores are empty
\( n_{rl} \): refractive index measured when pores are filled
\( n_{ads} \): refractive index of the solvent
Porosity measurement

\[ B_3 = \frac{n_{rl}^2 - 1}{n_{rl}^2 + 2} = V \frac{n_{ads}^2 - 1}{n_{ads}^2 + 2} + (1 - V) \frac{n_2^2 - 1}{n_2^2 + 2} \]

\[ B_2 = \frac{n_{re}^2 - 1}{n_{re}^2 + 2} = (1 - V) \frac{n_2^2 - 1}{n_2^2 + 2} \]

Therefore,

\[ V = \left( \frac{n_{rl}^2 - 1}{n_{rl}^2 + 2} - \frac{n_{re}^2 - 1}{n_{re}^2 + 2} \right) / \left( \frac{n_{ads}^2 - 1}{n_{ads}^2 + 2} \right) \]

- \( n_{re} \): refractive index measured when pores are empty
- \( n_{rl} \): refractive index measured when pores are filled
- \( n_{ads} \): refractive index of the solvent

No need to know the refractive index of the skeleton

\( V \) is the volume of open pores
Measurement principle

Acquisition of SE spectra

Analysis of SE spectra:
Calculation of Thickness / Refractive index

Thickness vs partial pressure

Refractive index @ 633nm vs partial pressure
Measurement principle

Lorentz-Lorentz Equations

=> Solvent volume vs rel. pressure

Porosity = 31%
### Meso Pores: Kelvin

**Pore size with diameter form 2 to 50nm (IUPAC classification)**

The solvent is in a liquid phase

Pore radius: \( r = \frac{2\gamma V_L}{RT \ln(P/P_0)} \)

- \( Po \): equilibrium vapor pressure
- \( P/P_0 \): relative equilibrium vapor pressure above meniscus
- \( g \): Surface tension of adsorptive
- \( V_L \): molar volume of adsorptive
- \( r_h \): mean radius of curvature
- \( q \): wetting angle

**EP gives a distribution of pores for every relative pressure not a distribution a posteriori.**
Mesoporous material

From Solvent volume to Pore Size Distribution:
Hysteresis in the isotherms => mesoporous material (r > 1 nm)
The pore radius for the adsorption is 2.5nm (cavities) and the pore radius for desorption is 1.9nm (connections).
Microporous material

Micro pores: Dubinin Radushkevich
Pore size with diameter below 2nm (IUPAC classification)
The solvent is in a gas phase

\[
\frac{W}{W_0} = \exp\left\{ - \frac{RT \ln(P_0/P)}{(\beta E_o)^2} \right\}
\]

Pore radius: \( r = \frac{6}{E_o} \)

W/W_0: fractional filling of the micropore volume: W_0
\( \beta \): scaling factor (affinity coeff.)
E_o: characteristic energy
r: pore radius, nm, normal distribution, average radius

\[
\begin{align*}
\text{Ln}(V) & \quad \text{Ln}^2(p_0/p) \\
-6.36838614267765 & \quad 60.965412465549 \\
-4.67839007262632 & \quad 49.221408284231 \\
-5.16160802779383 & \quad 41.37245950233 \\
-5.21082991099096 & \quad 34.9376351838247 \\
-4.12715216177882 & \quad 26.8730040292041 \\
-4.0684111672946 & \quad 22.37662106353 \\
-3.63299473960852 & \quad 17.2037913967749 \\
-3.05876043728472 & \quad 11.4797802777917 \\
-2.76752532211873 & \quad 6.9058739520692 \\
-2.56657315455311 & \quad 4.17480130899704
\end{align*}
\]

Microporous total volume: 20.5%
Microporous percentage: 73%
Microporous average radius: 0.62 nm
Microporous material

Mesoporous volume: 3.5%

Mesoporous distribution calculated with kelvin equation

Microporous volume: 20%
Pore size: 0.75nm

- Total Porous Volume:
  microporous volume
  mesoporous volume
- Average pore size
- Pore size distribution

0.09
Why distribution is important

Same average density however different PSD

Random porosity  Periodic pore structure

Courtesy of Dr. Shirataka, Asahi Kasei Corporation
PSD control for best integration

Tail of the distribution is very important as PSD can lead to problems in the integration.

Low percentage of pores for R > 2 nm

Wide distribution
Exemple of porosity

36%, 1.8nm

28%, 1.1nm

12%, 1.0nm
Ultra thin Ultra low K: 600A

Porosity = 19.8%
Pore radius = 1.0 nm
**BDII - K = 2.5**

- **Open Porosity = 26.4%**
- **Pore Radius = 1.1 nm**

**PALS results:**
- **Porosity: 26.6%**
- **Pore radius: 1nm**
300mm Mapping

**EP features:**

- Small spot of 250x250um to achieve edge exclusion better than 2mm
- Field viewing camera
- Mapping stage for 300mm and 200mm
- Sites coordinates are recipe parameters

<table>
<thead>
<tr>
<th>Position</th>
<th>Thickness (µm)</th>
<th>Porosity (%)</th>
<th>Pore Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>295.8 ± 0.3</td>
<td>33.1</td>
<td>1.9</td>
</tr>
<tr>
<td>Left</td>
<td>296.0 ± 0.3</td>
<td>33.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Center</td>
<td>292.4 ± 0.7</td>
<td>32.8</td>
<td>1.7</td>
</tr>
<tr>
<td>Right</td>
<td>299.6 ± 1.0</td>
<td>34.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Bottom</td>
<td>299.4 ± 0.7</td>
<td>34.4</td>
<td>1.9</td>
</tr>
</tbody>
</table>
Sealing of porous materials

Sealing Techniques

Additive

- Plasma deposition
  - Ta/TaN
  - Dielectric
  - Polymer

- Atomic Layer Deposition
  - TaN
  - WCN
  - TiN etc.

- Wet Chemicals
  - Micelles
  - Silanols
  - Thiols
  - Siloxanes

Surface densification

- By plasma
- By e-beam
- By Giant Ion Clusters
- By UV

Source: M Baklanov - IMEC
Measurement on Pattern - sealing

Sample:
Trenches: lines of 140nm 1/1 ratio
SiO2 (250nm) /ULK (300nm) /SiC (50nm)

Continuous change in SE spectra during adsorption cycle.
The solvent fills in the materials inside the trench (through pore killers)
Measurement on Pattern - Sealing

The solvent fills the trenches at saturated pressure
Change in Tan Psi only for P/P0 close to 1.
The Solvent condenses on the trenches

Sample:
Trenches: lines of 140nm 1/1 ratio
Sio2 (250nm) /ULK (300nm) /SiC (50nm)
Pore sealing treatment is efficient

Change in Tan Psi only for $P/P_0 > 0.8$

Pore sealing treatment is not effective

Continuous change in Tan Psi
Pore sealing

The piece of wafer is placed in the vacuum.

Initial vacuum → 60 sec under Solvent vapor → 150 sec under Solvent vapor

The solvent diffuses only through the edge and not from the Top of the film. => The porous layer is sealed.
Pores Sealing

If the barrier is fully continuous, toluene cannot penetrate.

In the case of not fully dense barrier, toluene can penetrate through barrier pinholes and can be adsorbed by the Low K film.

60 sec under Solvent vapor

150 sec under Solvent vapor

=> The porous layer is NOT sealed.
Interconnectivity

Solvent penetration depth into a porous material should be proportional to square root of exposure time. It is known from diffusion theory [7] that the mean distance traveled by a diffusion front is described by the following equation:

\[ l = 2 \sqrt{\frac{Dt}{\pi}} \]

<table>
<thead>
<tr>
<th>Material</th>
<th>Porosity (%)</th>
<th>Mean pore size (nm)</th>
<th>Diffusion coefficients (cm²/sec)</th>
<th>( D_{tol}/D_{eth} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Micro</td>
<td>Meso</td>
<td>toluene</td>
</tr>
<tr>
<td>MSQ1</td>
<td>40</td>
<td>1.4</td>
<td>3.5</td>
<td>2.4×10⁻⁵</td>
</tr>
<tr>
<td>MSQ2</td>
<td>40</td>
<td>1.4</td>
<td>3.2</td>
<td>2.0×10⁻⁵</td>
</tr>
<tr>
<td>SiOCH pristine</td>
<td>7</td>
<td>1.3</td>
<td>n/a</td>
<td>1.4×10⁻⁷</td>
</tr>
<tr>
<td>SiOCH+2°HF</td>
<td>12</td>
<td>1.3</td>
<td>3.0</td>
<td>2.0×10⁻⁷</td>
</tr>
<tr>
<td>SiOCH+4°HF</td>
<td>25</td>
<td>n/a</td>
<td>3.5</td>
<td>1.8×10⁻⁶</td>
</tr>
<tr>
<td>SiOCH+6°HF</td>
<td>32</td>
<td>n/a</td>
<td>6.5</td>
<td>1.5×10⁻⁵</td>
</tr>
<tr>
<td>SiOCH+8°HF</td>
<td>37</td>
<td>n/a</td>
<td>9.1</td>
<td>3.6×10⁻⁵</td>
</tr>
<tr>
<td>Polymer</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>2.2×10⁻⁸</td>
</tr>
</tbody>
</table>

Source: Shamyrian, Maex, MRS2003

Young Modulus calculation

Acquisition of SE spectra

Analysis of SE spectra:
Calculation of Thickness / Refractive index

Fit of the curve with the Young – Laplace equation:
\[ T = T_0 - k \ln \left( \frac{P}{P_0} \right) \]
\[ K = \frac{T_0 RT}{V.E} \]
\[ V = \text{Volume of the solvent molecule} \]
Young Modulus calculation

Effect of nanoindentor on porous low K

Change of thickness is only 1.5% (negligible for PSD calculation)

EP Young Modulus is close to SAWS, BLS and Nanoindentor.
## Correlation to electrical K

<table>
<thead>
<tr>
<th>Sample 5</th>
<th>Thickness (nm)</th>
<th>Optical Index (633 nm)</th>
<th>Porosity (%)</th>
<th>Porosity Radius (Ads/Des)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low K</td>
<td>277.1 ± 0.8</td>
<td>n = 1.287 &amp; k = 0</td>
<td>31.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Silicon</td>
<td></td>
<td>n = 3.881 &amp; k = 0.019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 6</td>
<td>Thickness (nm)</td>
<td>Optical Index (633 nm)</td>
<td>Porosity (%)</td>
<td>Porosity Radius (Ads/Des)</td>
</tr>
<tr>
<td>Low K</td>
<td>295.2 ± 1.0</td>
<td>n = 1.241 &amp; k = 0</td>
<td>42.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Silicon</td>
<td></td>
<td>n = 3.881 &amp; k = 0.019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 7</td>
<td>Thickness (nm)</td>
<td>Optical Index (633 nm)</td>
<td>Porosity (%)</td>
<td>Porosity Radius (Ads/Des)</td>
</tr>
<tr>
<td>Low K</td>
<td>290.7 ± 1.0</td>
<td>n = 1.266 &amp; k = 0</td>
<td>36.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Silicon</td>
<td></td>
<td>n = 3.881 &amp; k = 0.019</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample 8</td>
<td>Thickness (nm)</td>
<td>Optical Index (633 nm)</td>
<td>Porosity (%)</td>
<td>Porosity Radius (Ads/Des)</td>
</tr>
<tr>
<td>Low K</td>
<td>302.1 ± 1.0</td>
<td>n = 1.323 &amp; k = 0</td>
<td>20.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Silicon</td>
<td></td>
<td>n = 3.881 &amp; k = 0.019</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Summary table

Micro porous

Meso porous

Bi modal
Conclusion - EP

1. EP gives quantitative, accurate and repeatable measurement for:
   - Porosity
   - Pore size distribution for meso, microporous and bi-modal distribution
   - Film thickness and refractive index
   - Mapping of this parameters
   - Small spot for edge exclusion control

2. EP gives qualitative information for the pore sealing treatment of ULK layers.
   - Measurement of blanket wafers
   - Measurement of patterned wafers
   - ULK behavior in a process integration scheme
"Low dielectric constant materials for microelectronics"
"Ellipsometric Porosimetry of Porous Low-k Films with Quasi-Closed cavities"
Mikhail R. Baklanov, Konstantin P. Mogilnikov, Jin-Heong Yim
MRS Spring Meeting, 12-16 April 2004, San Francisco, USA

"Nondestructive Characterization of a Series of Periodic Porous Silica Films by in situ Spectroscopic Ellipsometry in a Vapor Cell"
C. Negoro, N. Hata, K. Yamada, T. Kikkawa

"Description of the porosity of inhomogeneous porous low-k films using solvent adsorption studied by spectroscopic ellipsometry in the visible range"
A. Bourgeois, A. Brunet Bruneau, V. Jousseaume, N. Rochat, S. Fisson, B. Demarets, J. Rivory

"Investigation of the microporous structure of porous layers using ellipsometric adsorption porometry"

"Diffusion barrier integrity evaluation by ellipsometry porosimetry"

"Low dielectric constant materials for microelectronics"

"Porous Thin Film Metrology for Low-k Dielectric"
Extrait de NIST Semiconductor Microelectronics and Nanoelectronics Programs, July 03, pp 82-86

"Determination of Porosity of TiO₂ Films from reflection Spectra"
T. Matsubara, T. Oishi and A. Katagiri
J. of the ECS, 149 (2), 2002, pp C89-C93
For more product information:
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