Porosity and Pore Interconnectivity Characterization and Understanding Using Positron Annihilation Lifetime Spectroscopy, Ellipsometric Porosimetry and X-ray Reflectivity

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Introduction

Considerable attention has been focused on exploring novel low dielectric constant (k) materials to replace the traditional interconnect dielectric material, silicon oxide, in order to reduce power consumption and capacitive signal delay from the back end of line(BEOL). It has been generally agreed that after first generations of dense low-k dielectrics, decreasing material density by incorporating porosity is the most feasible means to achieve ultra low k below 2.5. One popular way of introducing porosity is by a subtractive process, where a sacrificial chemical, or porogen, will decompose in post thermal treatment and generate voids within SiCOH skeleton. However, when a higher portion of porogen is introduced during deposition, pores tend to aggregate and interconnect, especially when porosity is above percolation threshold. The pore interconnectivity may lead to degradation of mechanical and thermal properties and permit intrusion of moisture, chemical species and sequestering of cleans byproducts. Therefore, **characterization and understanding of porosity and pore interconnectivity** are important to design and optimize porous low-k materials.

In this work, three non-destructive porosimetry techniques, ***Positron Annihilation Lifetime Spectroscopy (PALS), Ellipsometric Porosimetry (EP) and X-ray Reflectivity (XRR),*** are applied to characterize porous SiCOH low-k dielectric thin films of different porosity and pore interconnection, results will be analyzed and compared to highlight their pertinence for characterization micro-porous low-k materials.

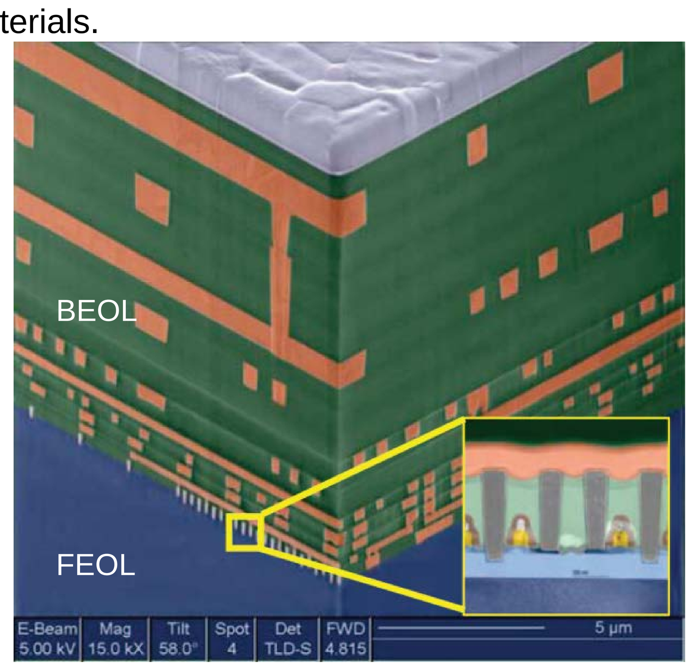


Figure 1 : Cross-sectional view of an IBM 90nm microprocessor[1]

$$\frac{k-1}{k+2}=\frac{4\pi}{3}N\left(\alpha_e+\alpha_d+\frac{\mu^2}{3k_bT}\right)$$

Equation 1: Dielectric constant defined by Debye equation

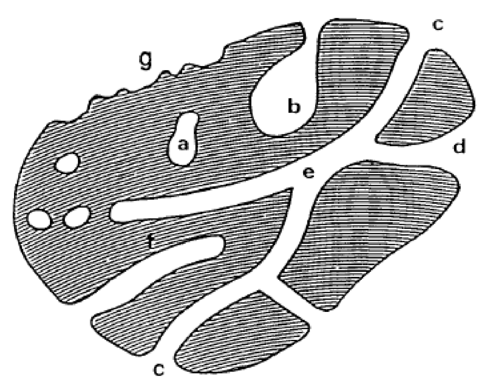


Figure 2 : Schematic cross-section of porous structure composed of pores of various shape and interconnection;[2]

Positron annihilation lifetime spectroscopy (PALS)

Positron annihilation lifetime spectroscopy (PALS) is a radiation based porosimetry. Ps localizes in pores and it annihilating lifetime will be reduced from its natural lifetime due to the collision with the pore surfaces. The Ps lifeitme can be correlated to the pore size and size distribution. A particularly powerful feature of PALS is the ability to perform depth profiling to determine interconnection length.

- **Total Ps intensity is indicative of porosity(A>C>B)**
- **F_{escape} suggests pore structure and interconnectivity (A>C>B).**
- **Pore radius can be derived from annihilation lifetime fitting: bimodal distribution of sample B**
- **Pore interconnection length for sample C is as 17nm**

Table 1: Summary of PALS results; Ps intensity, F_{escape}, pore radius and interconnection

	Sample A	Sample B	Sample C
Dielectric constant	2.0	2.2	2.4
Total Ps intensity (%)	34 ①	8 ③	24 ②
F_{escape} (%)	98.2 ①	0 ③	32.5 ②
Pore radius (nm)	2.4	0.75 &2.2	1.7
Pore interconnection	Fully percolated	bimodal pore distribution; Isolated pores	Pore interconnected over 17nm

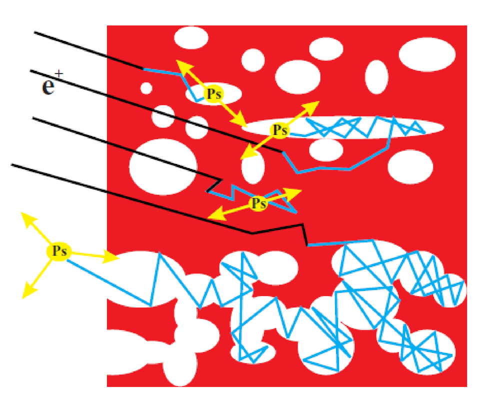


Figure 3: Schematic of Ps formation and escape in pores of different connectivity

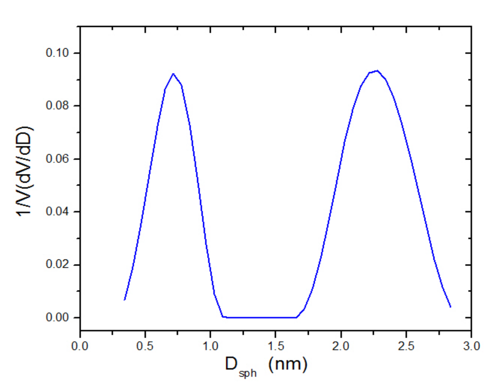


Figure 4: Bimodal pore size distribution of sample B

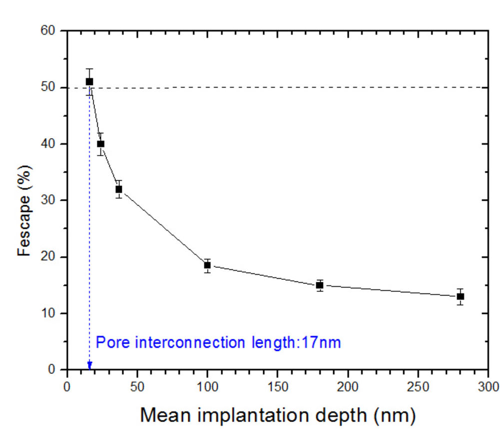


Figure 5: Ps escape fraction (Fesc) as a function of mean positron implan-ation depth used to calculate interconnection length (L_{int})

Ellipsometric porosimetry (EP)

Ellipsometric porosimetry is a adsorption-based porosimetry examining absolute porosity and pore size distribution (PSD). It utilizes the change of optical properties to monitor the amount of absorbent absorbed/condensed in pores (shown in Equation 2), which overcomes the poor sensitivity of traditional porosimetry when sampling small volumes. Toluene is used as the absorbent. Adsorption and deposition isotherms are acquired by stepwise raising relative pressure of toluene and recording the corresponding refractive index.

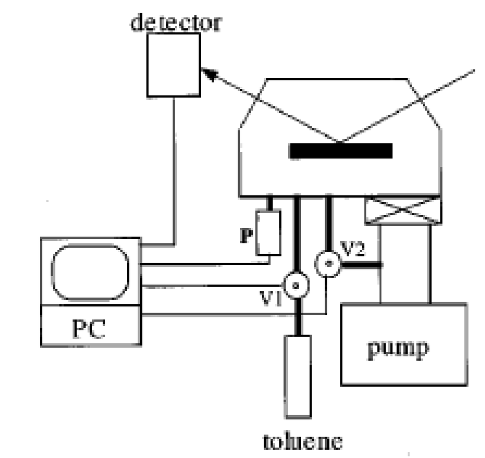
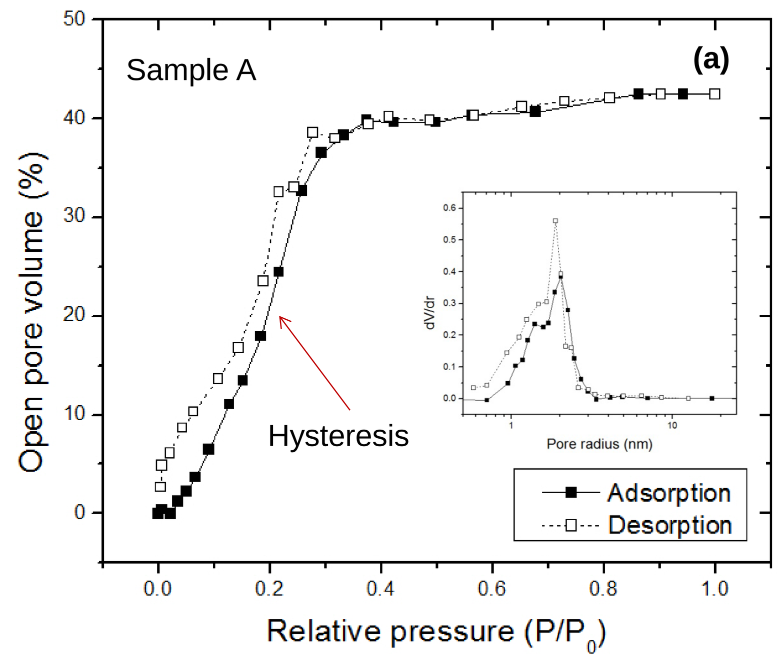
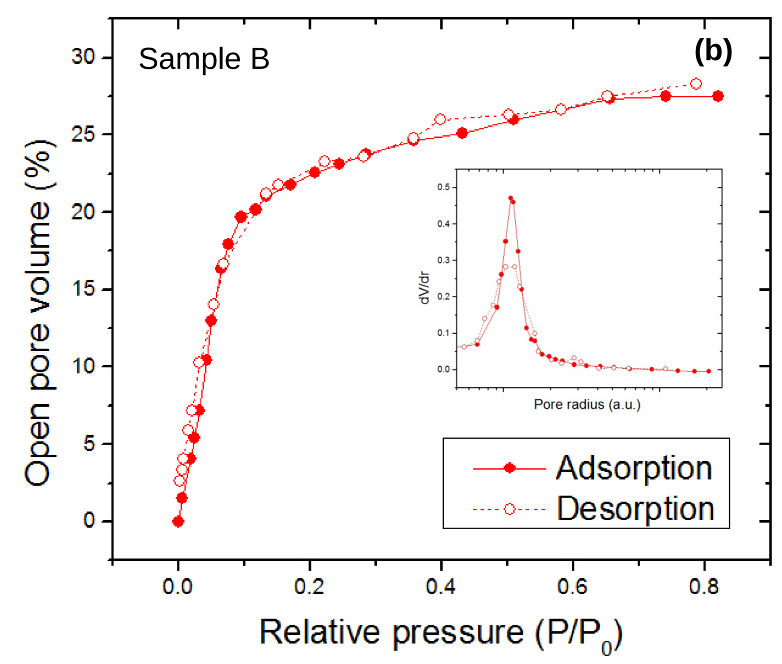


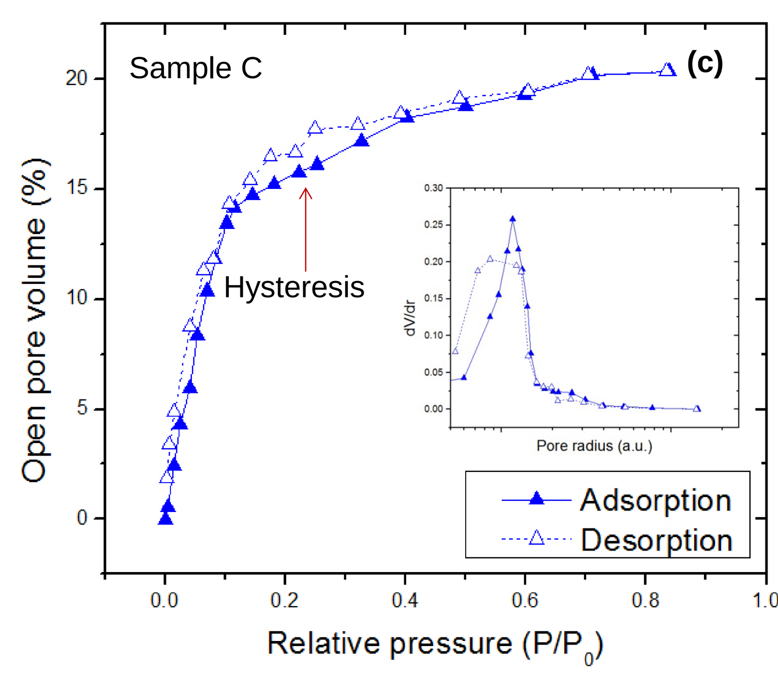
Figure 5: Schematic of EP configuration; an Ellipsometry equipped with vacuum chamber , absorbent and exhaust

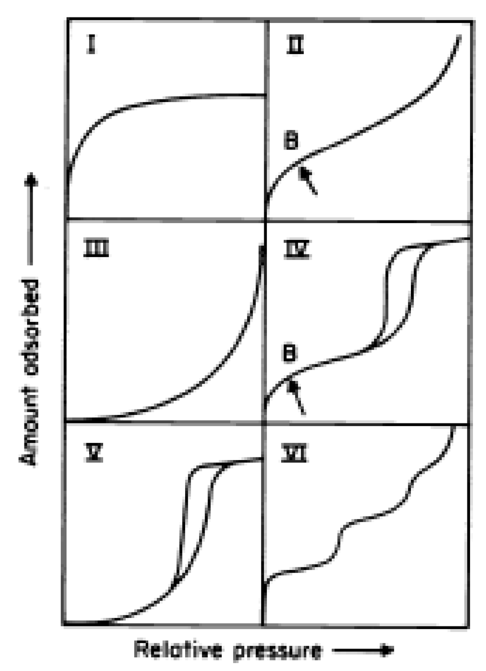
$$V=\left(\frac{n_{\mathrm{eff}}^2-1}{n_{\mathrm{eff}}^2+2}-\frac{n_{\mathrm{p}}^2-1}{n_{\mathrm{p}}^2+2}\right)\Bigg/\left(\frac{n_{\mathrm{ads}}^2-1}{n_{\mathrm{ads}}^2+2}\right)$$

Equation 2: Open pore volume defined by effective refractive index(RI) n_{eff}, RI of absorbent, and initial RI with empty pores.









- •Ⅰ. microporous solids;
- •Ⅱ. a non-porous or macroporous;
- •Ⅲ. adsorbate-adsorbate interactions;
- •Ⅳ. Capillary condensation;
- •V: Weak adsorbate-adsorbate interaction
- •Ⅵ. multilayer absorption

International Union for Pure and Applied Chemistry :IUPAC

Figure 6. Adsorption and desorption isotherm and corresponding pore size distribution of sample (a). A; (b). B; (c).C; (d). Characteristic isotherm defined by International Union of Pure and Applied Chemistry (IUPAC)

	Isotherm feature	Pore structure characteristics
Sample A	Hysteresis	Meso-porous with well-defined pore structure
Sample B	Pore filled at low relative pressure	Micro-porous with narrow pore size distribution
Sample C	Pore filled at low relative pressure; hysteresis	Bimodal distribution of both micro- and meso-pores; may contain necking structure

X-ray Reflectivity (XRR)

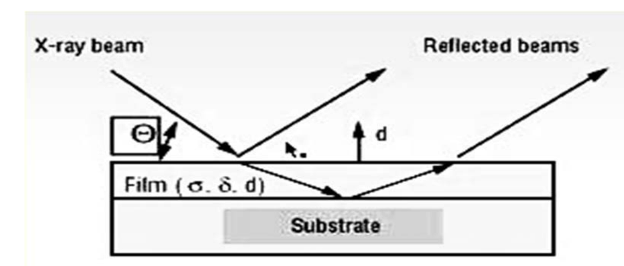


Figure 7: Schematic of total reflection occurred at critical angle with film on substrate structure

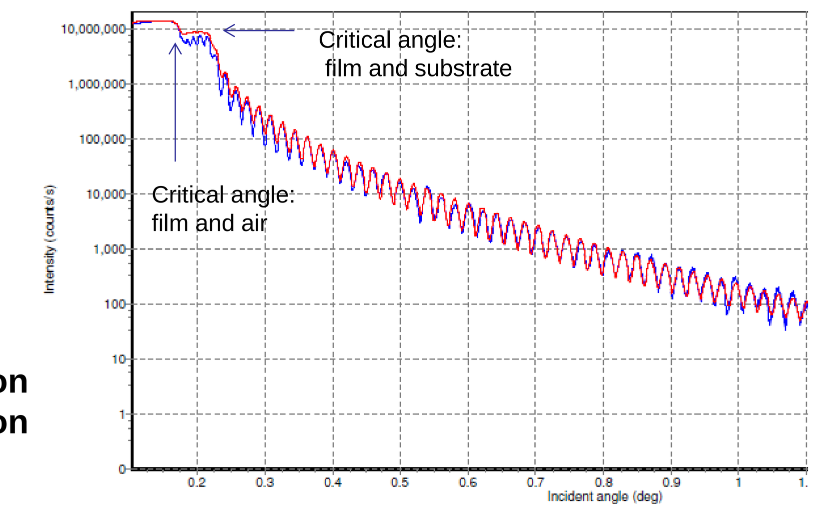


Figure 8: Example of reflectivity data for porous lo-k thin film deposited on silicon substrate

Sample	A	B	C
Estimated bulk film density (g/cm³)	1.7944	1.8393	1.8714
porous film density (g/cm³)	0.978	1.382	1.33
pore volume (%)	46	25	29

Table 2: Pore volume calculated by normalizing measured XRR film density over bulk film density estimated from stoichiometry

Comparison: PALS, EP and XRR

	Porosity/%			Pore radius/nm	
	PALS	EP	XRR	PALS	EP
Sample A	①	42	46	2.4	2.0
Sample B	③	27	25	0.75 & 2.2	2.1
Sample C	②	20	29	1.7	2.1 &3

Table 3: Porosity and pore radius comparison of PALS, EP and XRR results

	Strength	Limitation
PALS	• Able to detect pore size down to 0.3nm • Pore size distribution for non-percolated pores • Pore interconnectivity derived from depth profile	• Do not characterize absolute porosity • Do not provide PSD on percolated pores
EP	• Provide pore size distribution derived from isotherm • Provide absolute porosity • Able to distinguish multi-modal distribution	• Inaccessible to closed pores • Swelling may interfere porosity calculation
XRR	• Straightforward porosity derivation from material density	• Porosity calculation depends on bulk density assumption • Lack pore structure detail

Conclusions

In this work, porous low-k thin films of various porosity and pore interconnectivity are characterized using three types of porosimetry depending on different physical principles, Positron Annihilation Lifetime Spectroscopy (PALS), Ellipsometric Porosimetry (EP) and X-ray Reflectivity (XRR), in order to study the advantages of each technique. PALS is able to detect small pores and evaluate pore interconnectivity but not able to estimate absolute porosity or distinguish multi modal PSD of percolated pores. EP provides absolute porosity as well as PSD of isolated and percolated pores but is not accessible to closed pores. XRR estimates porosity in terms of material density but pore structure information is limited.

Acknowledgments

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