

Calculation of Pore Size Distributions in Low-k Films

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Abstract. Porosimetry is a key technology for the characterization of porous low-k dielectric films. A critical appraisal of the models used for quantitative interpretation of vapor adsorption isotherms obtained by ellipsometric and x-ray reflectivity measurements shows that conventional macroscopic methods based on the Kelvin equation are inadequate on the nanoscale. We have developed an advanced molecular model of toluene adsorption in nanopores and the method for pore size distribution calculations based on this model. The method has been verified against reference ordered porous silicas and applied to selected low-k films. Significant deviations of the Kelvin equation were found for pores < 4 nm. The new method provides a unified framework for reliable calculations of micro- and mesopore size distributions. The results are generally consistent with available data of small angle neutron scattering porosimetry.

Keywords: porosimetry, adsorption, pore size distribution, toluene, SANS.

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INTRODUCTION

Low-k dielectrics with nanoscale porosity are of great importance to the semiconductor industry [1, 2]. Accurate characterization of pore size distribution (PSD) and pore interconnectivity remains a topical problem. The standard methods of nitrogen or argon porosimetry do not provide enough sensitivity to measure adsorption in thin films [2-4]. Ellipsometric [3] and X-ray reflectivity [4-6] methods have been developed to measure adsorption/desorption isotherms of organic vapors (e.g. toluene) in thin films.

However, quantitative interpretation of vapor adsorption/desorption isotherms in terms of PSDs is challenging because: 1) Conventional methods are based on macroscopic Kelvin equation of capillarity [7], which does not account for solid-fluid interactions, and breaks down at the nanoscale [8-10]; 2) Suitable pore structure standards are lacking.

In this work we demonstrate that new approaches based on a combination of molecular-level pore models and experiments with reference nanoporous materials improve the accuracy of thin film porosimetry. We give a critical appraisal of adsorption models used to interpret adsorption isotherm

measurements and describe the development of a molecular-based method for calculating PSDs from toluene adsorption isotherms.

OVERVIEW OF EXISTING METHODS

Conventional methods of pore size characterization are based on equilibrium adsorption measurements interpreted in terms of classical thermodynamics of capillarity [7]. The Kelvin equation is exact in the limit of large pores, but it becomes progressively inaccurate as the pore size decreases and interactions of fluid with the pore walls become important. As a result, errors in the pore size of up to 100% may arise when the Kelvin equation is applied to nanosize pores. Adsorption-desorption hysteresis also introduces significant uncertainty in the PSD analysis. Conventional methods usually give different results when applied to the adsorption and desorption branches of the isotherm (see e.g. [3, 11]).

When the pore dimensions become comparable with the probe molecule, the macroscopic capillarity concepts are no longer valid. This is most problematic because porous low-k dielectrics have pore diameters in the range of only several nanometers. Moreover, the framework itself often contains micropores (pores < 2

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nm according to IUPAC classification). Current methods for micropore size calculations (<1nm) employ DR (Dubinin-Radushkevich) equation [7]. DR equation, which is purely empirical, was first suggested and validated for activated carbons. Its utilization for low-k dielectric materials [11] is questionable, however a proper choice of input parameters may give satisfactory results. The problem of correct characterization of pores within the size range of 1-4 nm is the key problem, since neither Kelvin nor DR methods are applicable in this scale interval.

Rigorous and significantly more accurate interpretation of the experimental adsorption-desorption isotherms in nanoporous materials can be achieved based on a molecular-level modeling and understanding of capillarity in nanoconfinements. Statistical thermodynamics models, such as nonlocal density functional theory (NLDFT) and Monte Carlo (MC) simulations, are capable of providing a unified description of adsorption in both micro- and mesopores.

In our recent publications [10, 12, 13] we have developed and experimentally verified NLDFT and MC based methods for pore structure characterization from gas adsorption isotherms. The methods have been verified on ordered templated nanoporous silicas. These materials possess highly ordered cylindrical or cage-like (near-spherical) pores with narrow PSD. At present, they are the best available references for adsorption studies and comparison with the theoretical models without invoking adjustable parameters – a unique opportunity which had not existed until only few years ago.

ADSORPTION ON REFERENCE MATERIALS

Reference materials with well-characterized pore structures are indispensable for standardizing adsorption measurements and calibration of adsorption porosimetry methods. We used highly-ordered reference MCM-41 and PHTS silicas. The mesopore structure of MCM-41 silica consists of an array of parallel cylindrical pores, arranged in a hexagonal lattice [14]. In MCM-41 the pores are not interconnected and the framework does not contain micropores (< 2 nm). The pore wall structure is similar to that in amorphous silicas. In PHTS (plugged hexagonal templated silica) [15] the pore walls are microporous, and thus permeable to small molecules, including toluene. In addition, some mesopores in PHTS contain constrictions or plugs. This creates a

system of open (from one or both ends) and blocked (closed from both ends but permeable through microporous walls) cylindrical channels, which exhibit different mechanisms of desorption.

The pore diameters of reference silicas were established from a combination of x-ray diffraction, nitrogen, argon adsorption, and geometrical modeling of the structure. Complete details about the preparation and structure of the MCM-41 silica material are given in Ref. [8]. The structure of the material has been recently checked by X-ray diffraction and nitrogen adsorption measurements performed in two different laboratories.

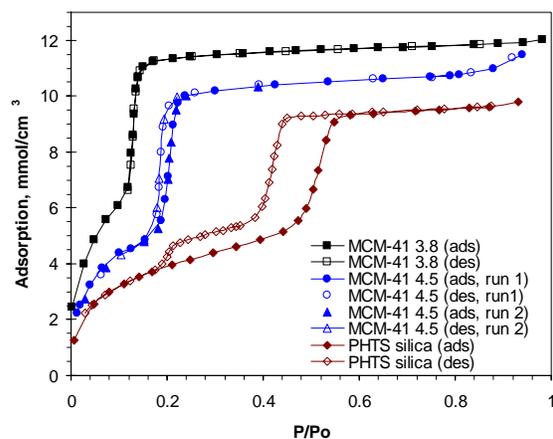


FIGURE 1. Toluene adsorption/desorption isotherms at 298 K on reference mesoporous silicas (see Table 1). For convenience, the vertical scale is shifted by 1 and 2 mmol/cm³ for samples MCM-41 4.5 and MCM-41 3.8, respectively.

Figure 1 shows the adsorption/desorption isotherms of toluene measured gravimetrically at 298 K (Carrot et al, unpublished). The isotherms on 3.8 and 4.5 nm MCM-41 materials feature the region of mono- and multilayer adsorption on the pore walls (below the relative pressure $P/P_o \approx 0.1-0.15$) followed by a sharp pore filling step. For the smaller pore diameter MCM-41 the step is completely reversible, and the adsorption branch coincides with the desorption one. As the pore diameter increases, a hysteresis loop develops. The hysteresis loop is of type H1, according to IUPAC classification [7], which corresponds to materials with open cylindrical pores. It is important to note that the curvature of the isotherms at low relative pressure (below $P/P_o=0.15$) is associated with the formation of a monolayer rather than with the micropore filling.

PHTS silicas are microporous. Therefore, the curvature of the isotherm at low pressures is associated with micropore filling and with monolayer adsorption on the pore walls. Separation of the two mechanisms

can be achieved by using a careful interpretation of the isotherm using molecular level models of the adsorption process in both micro- and mesopores [16]. This is important because many low- k dielectric materials are microporous.

PHTS silica exhibits a two-step desorption branch which reflects two different mechanisms of desorption [15]. The first step is associated with desorption from open cylindrical pores. The substep at $P/P_0=0.2$ is due to desorption from blocked cylindrical channels. These channels empty by a different mechanism than open cylindrical pores. Desorption from open cylindrical pores is an equilibrium process while desorption from blocked pores is determined by the size of the constrictions. If the constrictions are sufficiently wide, desorption occurs by the equilibrium mechanism. In the case of PHTS, however, constrictions are narrow, and desorption occurs by *cavitation* in the stretched metastable toluene confined within blocked mesopores. The pressure of cavitation does not reflect the size of the constrictions or pore itself [17].

It should be noted that the mechanisms of toluene adsorption/desorption are in perfect agreement with our recent theoretical [12], experimental [17] and molecular simulation [18] studies of adsorption-desorption hysteresis of N_2 , Ar and Kr in materials with open and blocked pores. It is also worth noticing that adsorption/desorption isotherms of toluene on some porous low- k films containing relatively large voids also exhibit a desorption step at $P/P_0=0.2$ [19] due to cavitation.

CALCULATION METHODS

Molecular Model of Toluene Adsorption

Monte Carlo simulations were performed using the united-atom model by Wick et al [20, 21]. In this model, seven interaction centers correspond to seven carbons of toluene molecule while hydrogens are accounted for implicitly. Atom-atom interactions were described by the Lennard-Jones potential with molecule-molecule cutoff at 9.7\AA . We checked by simulations that this approach reproduces very reasonably the saturated vapor pressure of toluene at 300K (4.07kPa versus 4.17kPa in experiment), but overpredicts the liquid density by 6% (0.91g/cm^3 versus 0.86g/cm^3 experimental value).

The pores were modeled as infinitely long cylindrical channels. Solid-fluid interactions were represented by an integrated Lennard-Jones (LJ)

potential imposed by the structureless cylindrical layer of oxygen atoms [22] onto each carbon atom of toluene molecule. We used identical solid-fluid potential for all seven carbons. However, this model is unable to predict adequately the sorption isotherm of toluene on silica surface in the monolayer region, because it doesn't account for the heterogeneity of the surface. For this purpose, we introduced attractive and repulsive centers randomly distributed over the surface. Each center was spherical in shape and it created a smooth square-well potential of 3.7\AA in diameter and between -3.33 to $2.64 kT$ in depth (per molecule). Using this model, we obtained a very good agreement between simulated and experimental isotherms on reference silica materials (Figure 2).

Sorption isotherms were calculated using standard grand canonical MC (GCMC) method [23]. In mesopores, where capillary condensation occurs, the pressure of vapor-liquid equilibrium was evaluated using the gauge cell method developed in our earlier work [24]. At each given pressure we performed ca. 450000 trial insertions, removals and displacements of per toluene molecule. Equilibration was performed over the last 300000 such steps.

Calculated equilibrium isotherms in model cylindrical pores showed good agreement with reference desorption isotherms on MCM-41 materials (Figure 2). For comparison, the density of toluene has been reduced by 6 percent to compensate for the higher bulk density in the model. It is seen that the model provides quantitative description of toluene adsorption in the complete range of relative pressures.

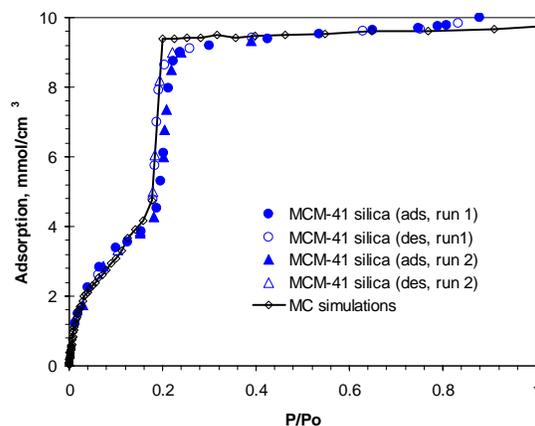


FIGURE 2. Experimental and MC simulated isotherms of toluene at 298 K on reference MCM-41 silica with cylindrical pores of 4.5 nm in diameter. The obtained pore volume of MCM-41 is $0.61 \text{ cm}^3/\text{g}$.

It should be noted that toluene adsorption is sensitive to the surface chemistry of the material. This implies

that toluene adsorption on organo-silica surfaces (e.g. silsesquioxane based films) might be somewhat lower than adsorption on pure silica surfaces. Further studies are required to assess how this would quantitatively affect pore size characterization.

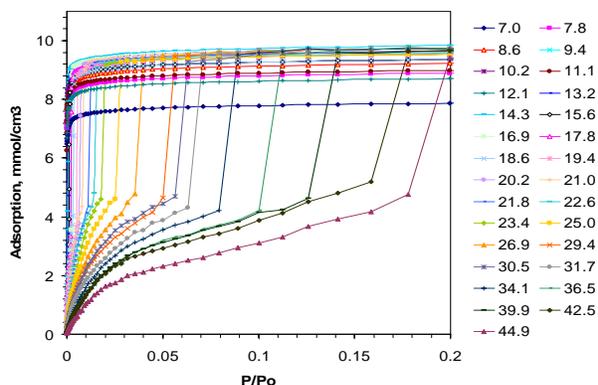


FIGURE 3. Adsorption isotherms of toluene in cylindrical pores at 298 K simulated by grand canonical Monte Carlo. The pore diameters in Angström are shown on the right.

Pore Size Distribution Calculations

Using the model developed we calculated sorption isotherms in pores with diameters ranging from 7 to 45 Å. The kernel of MC isotherms is shown in Figure 3. The isotherms feature pore filling steps which gradually shift to lower pressures as the pore diameter decreases. The PSD is determined from the generalized adsorption equation, which represents the experimental isotherm as a weighted sum of the theoretical isotherms in pores of different diameters:

$$N_{\text{exp}}(P/P_0) = \int_{D_{\text{min}}}^{D_{\text{max}}} N_{\text{theor}}(D, P/P_0) \varphi(D) dD \quad (1)$$

Here $N_{\text{theor}}(D, P/P_0)$ is the kernel of theoretical isotherms; $\varphi(D)$ is the PSD function. This approach is applicable to both unimodal and multimodal distributions. Solution of the integral equation (1) requires regularization methods, which are described in Refs. [25, 26]. From the practical point of view, the method for calculating PSDs is very fast because the kernel does not need to be recalculated every time new data is analyzed.

For the purpose of PSD calculations in a wider range of pore diameters, we created a hybrid model, which combines the MC isotherms for pores smaller than 4.5 nm and isotherms calculated by the Derjaguin-Broekhoff-de Boer (DBdB) approach for

pores > 4.5 nm. DBdB model accounts for the fluid-solid interactions in terms of the disjoining pressure [13]. Details will be given elsewhere.

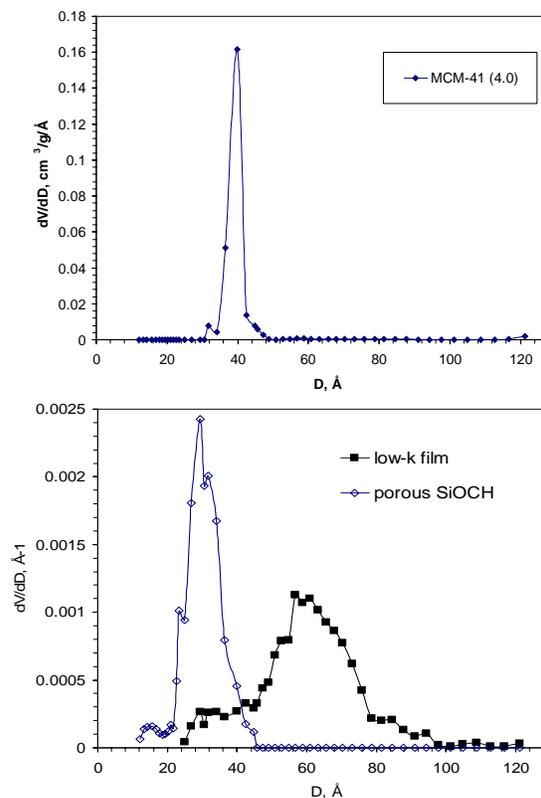


FIGURE 4. Pore size distributions of the reference MCM-41 silica (top) and two low-k samples (bottom). See Table 1.

EXAMPLES

Figure 4 shows PSDs calculated by the developed method. Very good agreement has been found for the pore sizes of reference silicas (Table 1). Macroscopic Kelvin equation based method significantly underestimates pore diameters due to its failure to account properly for the interactions of toluene with pore walls.

We have also analyzed literature data on selected low-k films. Figure 4 shows PSD calculated from toluene desorption isotherms measured by X-ray reflectivity method in Refs. [5, 27]. The isotherm for the low-k film reported in Ref. [27] exhibits type H2 hysteresis loop. Desorption occurs at $P/P_0=0.3-0.4$, i.e. above the cavitation pressure $P/P_0=0.2$. In this case the choice of the desorption branch for calculations assesses the size of constrictions in the porous matrix. This film has also been studied by small angle neutron scattering (SANS) porosimetry in Ref. [27]. We note

a good agreement between the average pore sizes determined from SANS and the present method (Table 1). This is in line with our recent results that adsorption porosimetry coupled with the molecular-

level interpretation of the isotherms gives quantitative agreement with the average pore sizes derived from SANS [28].

TABLE 1. Pore structure parameters of reference mesoporous silicas and low-k films

Sample	Pore diameter, nm	Pore diameter/Kelvin eq, nm	Pore diameter/developed model, nm
Reference PHTS silica	7.3 (meso) ^a , 1-2 (micro) ^a	6.5	7.3 (meso), 1.2-2 (micro)
Reference MCM-41 silica	4.5 ^a	3.4	4.5
Reference MCM-41 silica	4.0 ^a	2.9	4.0
Reference MCM-41 silica	3.8 ^a	2.8	3.9
Low-k film	6 - 8 (SANS) ^b	5.3 (des branch)	6.0 (des branch)
Porous SiOCH ^c	n/a	1.7	2.9

^a determined by X-ray diffraction, geometrical modeling, nitrogen and argon adsorption porosimetry

^b average pore size determined by SANS in Ref. [27]; ^c film described in Ref. [5]

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