



## Micro-imaging of liquid–vapor phase transition in nano-channels



Alexander Lauerer<sup>a</sup>, Philipp Zeigermann<sup>a</sup>, Jörg Lenzner<sup>a</sup>, Christian Chmelik<sup>a</sup>,  
Matthias Thommes<sup>b</sup>, Rustem Valiullin<sup>a,\*</sup>, Jörg Kärger<sup>a</sup>

<sup>a</sup> Faculty of Physics and Earth Sciences, University of Leipzig, Leipzig, Germany

<sup>b</sup> Quantachrome Instruments, Boynton Beach, FL, USA

### ARTICLE INFO

#### Article history:

Received 22 January 2015

Received in revised form

20 April 2015

Accepted 2 May 2015

Available online 11 May 2015

#### Keywords:

Phase transition

Capillary condensation

Sorption hysteresis

Porous silicon

IR microscopy

### ABSTRACT

Mesoporous silicon accommodating structured nano-channels is employed as a host material for recording the evolution of liquid–vapor phase transitions in nanoporous materials upon molecular adsorption and desorption. Analysis is based on the application of micro-imaging via IR microscopy revealing the spatial-temporal dependence of guest concentrations within the material as a function of the chosen pressure steps. In this way, phase transitions become observable in the context of their local environment and may be correlated with the pore architecture by immediate experimental evidence.

© 2015 Elsevier Inc. All rights reserved.

### 1. Introduction

In addition to temperature and pressure, the phase state of mesoporous host-guest systems is well known to depend on the system's history, that is, on whether the guest pressure in the surrounding atmosphere has been attained from lower or higher values, namely via ad- or desorption. This phenomenon is referred to as sorption hysteresis and serves, since more than a century, as a basis for estimating the pore sizes of such materials [1,2]. Phase state and pore geometry are, conceptually, correlated by the Kelvin equation [3].

$$\ln(p/p_0) = -\frac{2\gamma v}{rRT} \quad (1)$$

It indicates that, given a liquid phase with a meniscus of radius  $r$  within the pore space, this phase is at equilibrium with the surrounding gas phase at already a pressure  $p$  which is smaller than the saturation pressure  $p_0$  of the bulk liquid. The terms  $\gamma$ ,  $v$ ,  $R$  and  $T$  denote, respectively, surface tension, molar volume, the universal gas constant and temperature. Differences in the radius  $r$  of the meniscus at the transition from gas to liquid (capillary condensation, starting with a surface layer and, hence, an effective meniscus

radius of twice the pore radius) and from liquid to gas (capillary evaporation, with  $r$  approaching the pore radius) are immediately seen to correspond, via Equation (1), to different pressures. Equations correlating phase transitions with pore geometry have, since this time, been subject to continuous improvement concerning both microscopic fluid structure and phase equilibrium of confined ensembles [4–7]. The availability of ordered porous materials accommodating nano-cylindrical pores [8] made them particularly useful model systems for validating theoretical developments [9,10]. In increasing detail, the influence of the local geometric environment experienced by the guest molecules during phase transition has recently become a subject of intense studies [11–14]. The option to tailor pore geometry in a desired way is provided, among others, by electro-chemically etched mesoporous silicon [15,16] allowing to produce nano-cylindrical pores with purposefully varied pore diameters [17–20]. In this way, for the first time the influence of pore hierarchies and their arrangement on phase transition could have been subject to direct investigation. Stimulated by a continuously increasing diversity of nanoporous materials, efforts to improve the correlation between pore architecture and phase transition have thus, up to date, remained a topic of intense research [21–24].

About the rate of these transitions and their intrinsic mechanisms, however, there is still little known [25–29]. This deficiency in our knowledge is mainly related to the lack of experimental data

\* Corresponding author.

E-mail address: [valiullin@uni-leipzig.de](mailto:valiullin@uni-leipzig.de) (R. Valiullin).

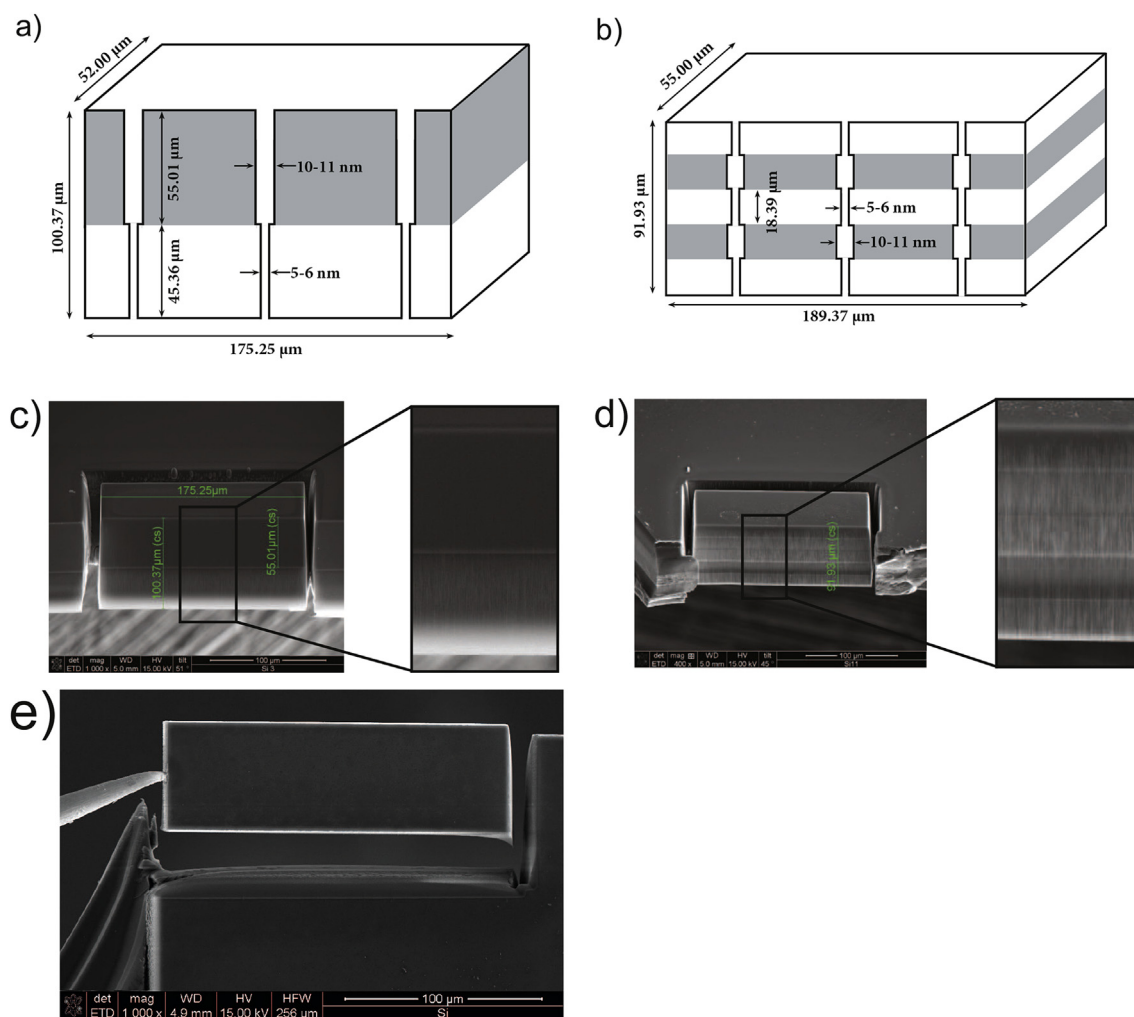
correlating the rate of equilibration with the pore structure. Whilst the system's response to pressure variation outside hysteresis is well-known to be governed by molecular diffusion, with equilibration over well-defined and easily predictable time scales [30], uptake and release within the range of hysteresis are found to be dramatically slowed down [20,27,31,32]. First quantitative studies of this retardation have been performed with Vycor porous glass, using the NMR signal intensity as a measure of the overall amount of guest molecules [27]. However, neither the technique of measurement nor the system under study allow, by their very nature, to directly correlate the changes thus observed with the systems pore structure. Here we report of how electro-chemically etched mesoporous silicon was successfully applied to provide exactly this information by micro-imaging via IR microscopy [33].

## 2. Experimental results

Fig. 1 introduces into the mesoporous host systems considered in this study. As a starting material for both systems under study, single-crystalline  $\langle 100 \rangle$  oriented p-type silicon wafers were used.

By tuning the current density and the time of etching, the pore size and length of the etched channels were adjusted to give rise to the two channel geometries, represented schematically in Fig. 1a and b and, by electron microscopic images, in Fig. 1c and d. Details about the preparation procedure are contained in the Supporting Information (SI). As a precondition for micro-imaging by IR microscopy, platelets with side faces parallel to the direction of the nano-channels had to be cut out of the silicon wafers. This was accomplished by using a focused beam of  $\text{Ga}^+$  ions for well-positioned silicon sputtering, using  $\text{XeF}_2$  for gas-assisted etching and to evacuate waste products. Subsequently, by means of a piezo-steered needle (Fig. 1e), the platelets were positioned within the IR cell.

IR micro-imaging was accomplished by means of a Fourier-transform IR microscope (Bruker Hyperion 3000) [34]. The use of a focal plane array (FPA) detector allowed the observation of guest distributions with a spatial and temporal resolution of about  $10 \mu\text{m}$  and 90 s, respectively. Complementary measurements with improved temporal resolution were performed with a single-element detector (SE) yielding the total amount of guest



**Fig. 1.** Sketch of the two silicon cuboids under investigation with their corresponding dimension. Fig. 1a shows the sample with one 5 nm pore section continued by one 10 nm pore section. Fig. 1b illustrates the sample with three 5 nm and two 10 nm pore sections arranged in an alternating fashion. In each case three channels are visualized exemplarily and idealized in a schematic way (not true to scale). The channels proceed from top to bottom and are open on both sides. As well shown are electron microscopic images depicting the side view on the silicon cuboids with two pore sections (1c) and five pore sections (1d) prepared by ion beam milling, together with zoom-in views of the etched mesoporous layers. The different layers with either 5 nm or 10 nm pores can be distinguished optically. Fig. 1e shows the view on top of a dissected porous silicon platelet attached to a piezo-driven needle within the sample chamber of the FIB (focused ion beam) setup. Subsequently, the sample was placed into an IR cell. In this view, the pores are directed perpendicular to the plane of observation.

Download English Version:

<https://daneshyari.com/en/article/72550>

Download Persian Version:

<https://daneshyari.com/article/72550>

[Daneshyari.com](https://daneshyari.com)