



Pore analysis of obliquely deposited nanostructures by krypton gas adsorption at 87 K

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ABSTRACT

The porous nature of high surface area and large aspect ratio nanorods arrays make them strong candidates for a range of applications from catalyst supports to energy scavenging devices. The glancing angle deposition (GLAD) technique is a straightforward and flexible method for ensuring control of morphology and porosity in nanorod arrays. Quantifying the porous nature of nanostructured columnar arrays, fabricated using the GLAD technique, is critical for understanding and optimizing the performance of devices fabricated using this method. The mesoporosity and pore volume of these GLAD nanorod arrays have thus been characterized using gas adsorption (krypton adsorption at 87.3 K) and scanning electron microscopy (SEM) image analysis techniques. To characterize the obliquely deposited amorphous titanium dioxide (TiO₂) and silicon dioxide (SiO₂) samples, top-down SEM images of the films were also analyzed which allowed us to determine the mean distance between columns. SEM image analysis permitted for estimation of inter-column porosity of films deposited at angles from 65° to 85°, while krypton analysis allowed for the identification of mesoporosity in films from 45° to 85°. Our results provide a comprehensive characterization of GLAD film porosity which will be vital for the design of devices for a diverse set of applications from photonics to sensing to microfluidics.

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1. Introduction

Porous oxide nanostructures are of great interest because they are widely used in a range of applications [1–5]. One approach to fabrication is the glancing angle deposition (GLAD) technique, a physical vapor deposition (PVD) method that employs substrate rotation and oblique incident vapor flux to create structures with characteristic columnar construction [6]. Because of the ease of which they are deposited and the variety of structures that can be fabricated, thin columnar films fabricated using the GLAD technique are becoming popular for sensing, microfluidic, optical, and solar devices [7–12]. This large application space makes the understanding of the fundamental properties of GLAD films crucial for optimizing device properties. Work has consequently been undertaken by a number of groups to understand how film properties such as density and anisotropy respond to deposition conditions such as the orientation of the substrate [10,13–15]. Characteristics such as surface area and growth scaling have also been studied for a number of deposition materials, including organics, metals and metal oxides [16–20]. In addition, roughness of GLAD films fabricated from materials such as platinum and chromium have

been determined by atomic force microscopy (AFM) [21,22]. While properties such as inter-column spacing have been examined for several obliquely deposited nanostructures [19], mesoporosity has been investigated by very few groups [18,23] and no data exists in the literature to describe the mesoporosity of metal oxide GLAD films. The optimization of devices using porous metal oxides, such as sensors, photonic crystals, photocatalysts, and solar cells, all rely on the precise knowledge of the structure's porosity. In this work we therefore expand on the understanding of the porous nature of titania (TiO₂) and silica (SiO₂) GLAD nanorod arrays. We have focused on TiO₂ and SiO₂ because of their wide use in applications such as microfluidic supports, optical coatings, and humidity sensors [9–11]. The understanding and control of porosity for metal oxide devices is important for controlling light scatter in optical devices, as well as for facilitating gas diffusion in sensors and molecule detection of various sizes in microfluidic instruments. To accomplish our goal of understanding the relationship between porosity and GLAD metal oxide deposition parameters, scanning electron processing (SEM) image analysis and a recently developed krypton gas adsorption technique have been employed.

The characterization of nanostructured powders or thin films can be carried out a number of ways, such as X-ray diffraction (XRD) [12,18] and ellipsometry [13,19]. However, physical adsorption (e.g. nitrogen and argon sorption at 77.4 and 87.3 K,

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respectively) is widely used for the surface area, pore size and porosity characterization of nanoporous materials [24–26]. For example, the Brunauer–Emmett–Teller (BET) method is commonly used to estimate the surface area of film and powder samples [27].

Over the last decade or so major progress has been achieved in porous materials characterization by physical adsorption, mainly because of (i) advances in experimental adsorption techniques, (ii) the development and application of microscopic approaches such as the density functional theory (DFT) of inhomogeneous fluids (and methods based on molecular simulation) which allows one to describe adsorption and phase behavior of fluids in pores on a molecular level, and (iii) the discovery of novel ordered nanoporous materials (e.g. MCM-41, SBA-15) which exhibit a uniform pore structure and morphology and could therefore be used as model adsorbents to test theories of gas adsorption [28–30]. It was found that by applying the methods based on DFT and molecular simulation for pore size analysis one could obtain accurate pore size information over the complete range of micro and mesopores (i.e. from 0.35 up to 100 nm), whereas classical methods such as the Kelvin equation-based methods (e.g. the Barrett–Joyner–Halenda (BJH) approach) lead to large systematic errors (e.g. the BJH methods underestimates the true pore size by up to 20–30%) [30–34].

Despite the advances in this area, the characterization of thin porous films remains difficult because convenient gas adsorption techniques involving nitrogen and argon at 77.4 and 87.3 K cannot be easily applied to this task [24,25]. Such films are typically only a couple of hundred nanometers thick and the application of nitrogen and argon adsorption is (because of the high saturation pressure of 101.3 kPa) not sensitive enough to detect the small pressure changes which occur during adsorption of the gas onto the thin film surface. Instead, despite the sorption measurement is performed far below the bulk triple point temperature, supercooled krypton at 77.4 or 87.3 K can be used as an alternative adsorptive. The saturation pressure of supercooled liquid krypton is 351 Pa, 1/300th that of nitrogen at liquid nitrogen temperature. Hence, krypton adsorption at these temperatures is much more sensitive and can be applied to assess surface areas down to at least 0.05 m², and is considered a standard method for low surface area analysis [24,25,34].

Pore size analysis based on krypton adsorption is problematic if classical macroscopic methods such as the Kelvin equation (and the correspondent BJH method) are applied, because one has to make assumptions concerning the thermophysical properties of the pore fluid (e.g. surface tension, liquid or solid density and contact angle) which are not defined for temperatures below the bulk triple point temperature and depend strongly on pore size and temperature. Furthermore, the Kelvin equation does not predict correctly the phase behavior of fluids in narrow mesopores, in particular at temperatures below the bulk triple point temperature. One has to take into account that the sorption and phase behavior of fluids in mesopores is affected by the shift of the phase diagram (i.e. critical point, triple point, freezing temperature, etc.) due to confinement [35–37]. It was found that, for instance, for argon at 77 K (which is 6.5 K below its triple point) pore condensation does not occur if the pore diameter exceeds 15 nm [38]. Similar sorption experiments with krypton at 77 and 87 K revealed that pore filling cannot be observed anymore in cases where the pore diameter exceeds ~6 and 9 nm, respectively [39,40]. Hence, even by assuming proper values with regard to the thermophysical properties of a confined pore fluid the Kelvin equation cannot predict the pore filling characteristics, if the pore size exceeds a critical value. Unfortunately, no methods for krypton pore size analysis based on density functional theory (e.g. NLDFT) and molecular simulation exists so far; hence, empirical approaches have been used to address this problem.

Within this context we apply in our study a novel empirical method which was developed by Thommes involving the adsorption of krypton at 87.3 K on highly ordered mesoporous molecular sieves of defined pore size (~2–10 nm) and geometry (such as MCM-41 and SBA-15) and correlation of the measured pore sizes and volume to those obtained by applying NLDFT methods to nitrogen (at 77.4 K) and argon (at 87.3 K) sorption isotherms obtained on the identical silica samples [41–43]. Hence, pore size obtained by application of this krypton adsorption method is traceable to NLDFT pore size analysis. Both capillary condensation and capillary sublimation can occur as a function of pore size at 77.3 K, whereas at 87.3 K vapor–liquid phase transitions occur up to close to the sublimation pressure of the bulk fluid [28]. This is a requirement in order to obtain a monotonically increasing relationship between the pore filling pressures and the pore size. The density of the krypton-phase confined in silica mesopores was obtained from the known pore volumes of these mesoporous molecular sieves and krypton sorption isotherms (i.e. krypton adsorption after complete pore filling) in these materials. By this method, an average value of 2.6 g cm⁻³ was obtained, which agrees well with the calculated density of supercooled liquid krypton (by extrapolation of the phase diagram of bulk krypton down to 87.3 K). Knowing the density of the confined krypton phase allows pore volumes of the thin films to be calculated. Although the suggested method was developed for silica materials, it should also be applicable to materials, such as our GLAD nanorod arrays, with a surface chemistry similar to siliceous materials, such as other metal oxides (e.g. titania, alumina, etc.).

2. Experimental methods

The details of GLAD thin film depositions carried out for the present study have been described in other work [16]. A summary of the sample preparation conditions are provided here. Amorphous TiO₂ (Cerac, 99.9% pure rutile) and SiO₂ (Cerac, 99.99% pure) structured thin films were deposited by electron-beam physical vapor evaporation (Axxis, Kurt J Lesker) onto cleaved pieces of 1 cm × 1.5 cm factory-polished silicon wafer (p-type ⟨100⟩, University Wafer). Through the use of computer-controlled substrate orientation (with samples deposited at fixed oblique angles (α) ranging from 0° and 45° to 85°) and rotation (0.1 rev nm⁻¹), as well as deposition rate (1 nm s⁻¹), vertical post films with a range of densities were deposited. The films deposited at 0° were used to estimate the density of a non-porous sample. To promote the correct TiO₂ stoichiometry, two steps were taken: during deposition O₂ gas was introduced (with pressure kept at 8 × 10⁻³ Pa) and after deposition the TiO₂ samples were annealed at 100 °C for 24 h [44–46]. In the case of the SiO₂

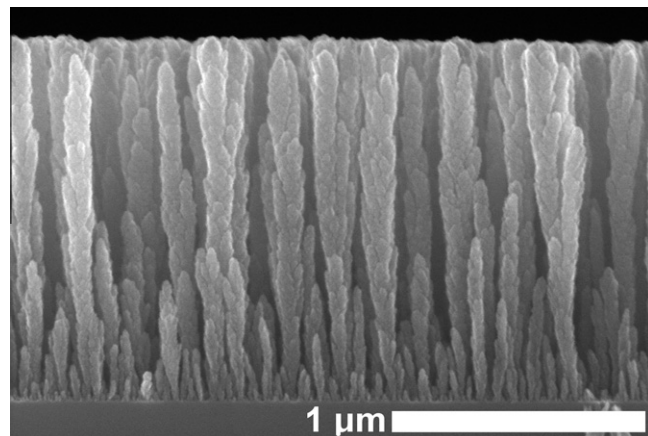


Fig. 1. SEM of representative TiO₂ GLAD vertical post samples, deposited at $\alpha = 85^\circ$.

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