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Surface roughness and chemical properties of porous inorganic films

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ABSTRACT

Porous inorganic films of different materials and pore architecture: mesoporous γ-alumina, mesoporous yttria stabilized zirconia (YSZ), macroporous YSZ and macroporous/microporous zeolite silicalite, were synthesized by the sol–gel spin-coating or dip-coating methods on silicon wafers of different surface roughness. Their surface chemical properties, pore and phase structure, and surface roughness were studied by various surface characterization methods. The pore sizes of these films are determined by their primary particle size. All the films studied are hydrophilic due to the presence of hydroxyl groups on the external crystallite surface, and their hydrophilicity increases in the order: macroporous YSZ < mesoporous YSZ < silicalite < γ-alumina. The γ-alumina films have highly smooth surfaces, while mesoporous YSZ, macroporous YSZ and silicalite films have similar surface roughness much rougher than γ-alumina films. The surface roughness of these coated films does not depend on the coating method, surface roughness of the substrate, surface chemistry or pore structure of the films. It is more controlled by the shape and size of the primary particles and aggregates in the sol or suspension from which the films are obtained.

1. Introduction

Macroporous and mesoporous inorganic films are obtained by packing metal oxide crystallites, with inter-crystalline space giving rise to the pores of the film. These porous films have been extensively studied as microfiltration or ultrafiltration membranes for separation applications [1]. They are used as supports for microporous and dense inorganic or polymer membranes [2,3] or even biological membranes [4,5]. In these applications, a thin microporous, dense separation layer or biologic film is formed on the surface of the mesoporous or macroporous inorganic supports, which provide the mechanical strength for the membrane layer or film while allowing transport of mass in molecular or ionic form. Recently, there is also an increased interest in developing batteries, especially lithium ion batteries, with improved safety characteristics and wider operation conditions [6]. Macroporous and mesoporous inorganic films offer potential for use as the separator in batteries to improve their performance [7,8]. In these applications, the porous inorganic film hosts the ionic conducting liquid electrolyte and separates the cathode and anode of the batteries.

Extensive studies have been conducted on synthesis and properties of macroporous and mesoporous inorganic thin films [1–3]. However, most studies regarding the properties of these porous films were focused on their gas and liquid adsorption, diffusion and permeation/separation properties. For application of these thin films as membrane supports or battery separators mentioned above, the surface roughness and surface chemical properties, in correlation with their pore structure, are important. The surface roughness of the macroporous or mesoporous films determines the thickness and quality of the membranes (or electrodes) that are formed in a device incorporating these films. The surface properties of these films influence the affinity and bonding of the film with the membrane layer or electrode. However, little information is available about the surface roughness of various porous inorganic films and its correlation to the surface chemical properties and pore structure.

This paper reports a study on the surface roughness in relation to the pore and phase structure and surface properties of the following four porous inorganic films: mesoporous–microporous zeolite (silicalite), mesoporous γ-alumina, mesoporous zirconia (doped with ~8 mol% yttria to stabilize its phase structure, referred to as yttria stabilized zirconia, or YSZ) and macroporous YSZ. The selection of these supports allows investigation into the effect of materials, surface chemistry and pore size of the thin films on the film surface roughness. Mesoporous and macroporous YSZ supports enable pore size to be examined, while sol–gel derived γ-alumina and mesoporous YSZ supports have very similar pore sizes but different surface chemistry. Thin films of MFI type zeolite silicalite exhibit hierarchical porosity with intrinsic crystalline micropores (ca. 0.6 nm) and mesopores resulting from

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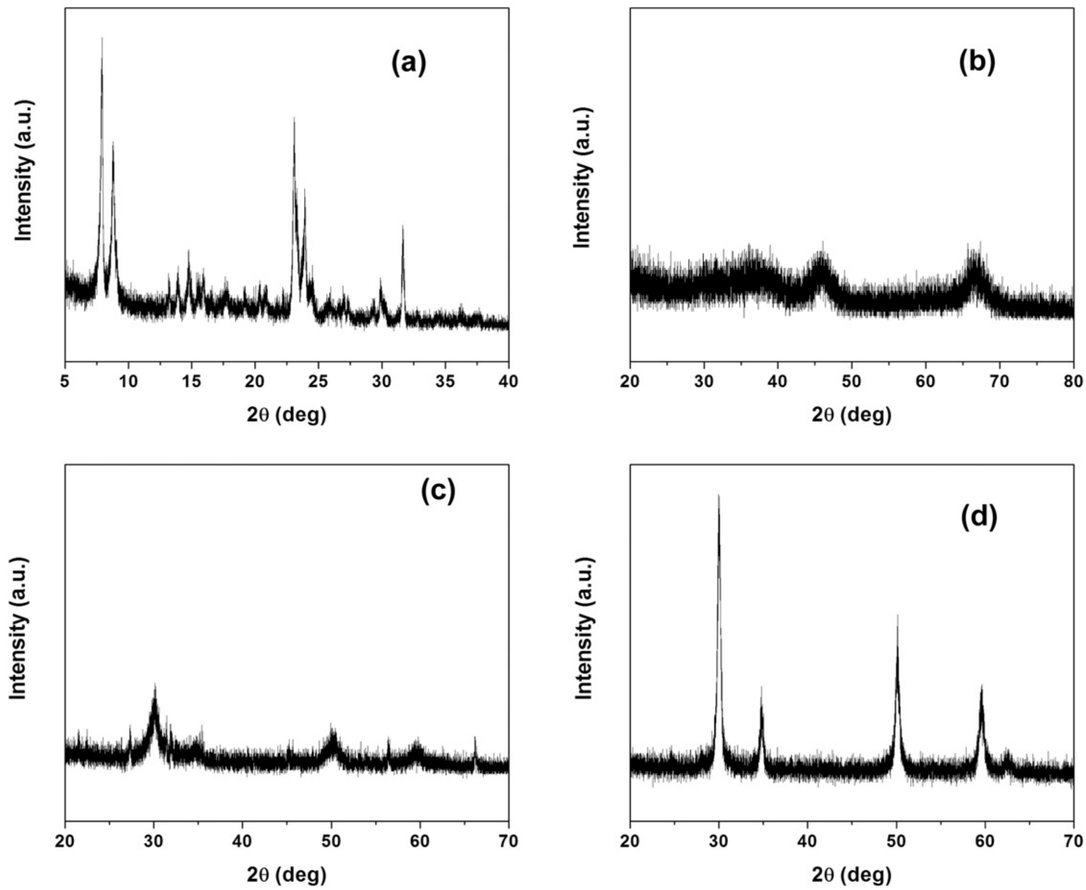

Fig. 1. XRD patterns of the powder used to make the substrate of (a) silicalite, (b) γ-alumina, (c) sol–gel derived (mesoporous) YSZ, and (d) suspension derived (macroporous) YSZ.

interstitial sites upon packing of the primary zeolite crystalline particles. This study is aimed at understanding key parameters that determine the surface roughness of these porous inorganic films.

2. Materials and methods

All thin porous films were prepared by spin-coating or dip coating of a sol (or suspension) containing particles of γ-alumina, yttria stabilized zirconia (YSZ), or MFI type zeolite silicalite. These sols or suspensions were synthesized by methods reported previously [9–12]. Stable γ-alumina (boehmite) sol was synthesized by hydrolyzing aluminum tri-sec-butoxide in water at 90 °C under refluxing conditions [9] to yield boehmite precipitate. The boehmite precipitate was peptized using nitric acid under reflux and heated to remove the excess alcohol. Prior to coating, the sol was mixed with a 3 wt.% poly(vinyl) alcohol (PVA, Fluka, $M_W = 72{,}000$ g/mol) aqueous solution to improve particulate binding after coating and prevent film cracking. Boehmite was converted to γ-alumina upon calcination at 400 °C after the formation of the film.

Table 1
Material properties of the inorganic thin films studied in this work.

Material	Phase structure	Pore diameter (nm)	BET surface area (m^2/g)	Water contact angle (deg)
γ-Alumina film	Cubic	~3.5	432	10 ± 1
Mesoporous YSZ film	Cubic	~4.0	28	35 ± 2
Macroporous YSZ film	Cubic	~50	14	38 ± 2
Silicalite film	MFI zeolite	~100, 0.6	225	21 ± 1

YSZ sols or suspensions consisting of YSZ particles of different sizes were prepared to produce mesoporous and macroporous YSZ films. For mesoporous YSZ films, zirconia sol was synthesized by adding zirconium (IV) n-propoxide (Alfa-Aesar) in isopropanol mixture to water dropwise at 70 °C [10]. The precipitate was filtered and washed several times to remove excess alcohol in the system. The precipitate was peptized in nitric acid overnight and diluted in water. 0.07 M yttrium (III) nitrate hexahydrate (Sigma-Aldrich) and a 3 wt.% PVA solution was added to the zirconia sol (in volume ratio of 3.2:1.3:1) to produce nano-sized YSZ particles. Macroporous YSZ films were prepared from YSZ suspension made by mixing micron-sized commercial YSZ powder (8 mol YSZ%, Tosoh) with nitric acid (pH = 3–4) (1:2 mass ratio) [11]. The suspension was ball-milled for one week to reduce the size of the micron-sized particles to about 200 nm. After ball milling, the solvent ratio was adjusted to yield a 10 wt.% suspension. The suspension was mixed with a 3 wt.% PVA solution (7:3 volume ratio) to improve particulate binding after coating and to prevent film cracking. Silicalite sols were synthesized with a molar composition of 10 SiO_2:4 TPAOH:1 NaOH:110 H_2O and hydrothermally treated at 125 °C for 8 h [12]. The spin coating solution was prepared by adding 0.5 wt.% hydroxyl propyl cellulose (HPC) (M_W 100,000 g·mol^{-1}, Aldrich) aqueous solution using Millipore water (18.2 MΩ) and titrating the suspension to pH 3–4 using 1 M HNO_3.

Three groups of thin porous films were prepared from the appropriate sol or suspension under different conditions on two different silicon wafers of different surface roughness's: (1) 1-inch standard silicon wafers with a 1 nm layer of SiO_2 on the surface occurring during air exposure, which gives a rougher surface, and (2) 8-inch silicon wafers (from ON Semiconductor) with a well polished, smooth surface. Ultrasonic mixing was applied to the sol or suspension before all coating procedures to minimize aggregation in the colloid systems. Group 1