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High-throughput fabrication of zeolite thin films *via* ultrasonic nozzle spray deposition

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ABSTRACT

Zeolite thin films with ordered nanopores and a low dielectric constant can serve as an insulation layer in microelectronic devices. However, the absence of a high-throughput deposition technique is a major technical hurdle in the industrial-scale production of zeolite thin films. Herein, we report on a scalable method, ultrasonic nozzle spray deposition (UNSD), which addresses this issue. A high-frequency standing wave introduced by the ultrasonic nozzle produces uniform sized droplets of the cast suspensions at a scale of tens to hundreds of micrometers, which results in a uniform thin film following the removal of the solvent. In this paper, we focus on the deposition of thin films comprising pure-silica zeolite MFI on a silicon wafer substrate. We systematically investigated how the quality of the zeolite thin films is affected by the composition of the cast suspensions and UNSD operating parameters. We identified the UNSD operating window that allows for the fabrication of uniform dense zeolite thin films at thicknesses ranging from hundreds of nanometers to 3 μm. We determined that zeolite MFI thin films prepared using UNSD outperformed those fabricated using conventional spin-on deposition in terms of uniform film thickness, low leakage current, and high Young's modulus.

1. Introduction

Zeolites are nanoporous crystalline aluminosilicates used in a broad range of industrial applications. Zeolite powders are generally processed into pellet form for use in catalysis [1–8] and adsorption [9–16]. Thin films and membranes comprising zeolites have opened up new possibilities for this class of materials in electronic devices [17–21] and membrane-based separations [22–30]. Various deposition techniques have been developed for the fabrication of zeolite thin films/membranes, including *in situ* growth [31–38], seeded growth [39–42], dry gel conversion [43–46] and dip coating [47–50]. Unfortunately, the incompatibility of these techniques with continuous production systems has greatly limited industrial-scale applications of zeolite thin films/membranes.

Wet deposition methods, such as spin-on deposition using a colloidal zeolite solution, have been developed to facilitate the large-scale fabrication of zeolite thin films [51–53], for use as anti-reflection films in optical devices [54] or as low-*k* films in electronic devices [55–64]. However, the quality of thin films prepared *via* spin-on deposition is highly sensitive to the colloidal properties of the cast solutions, such as the size of the zeolite crystals and the use of surfactant [55]. Defect-free MFI thin films can be produced only by sacrificing the overall crystallinity of the film [56]. Furthermore, despite the scalability of spin-on deposition, it is not easily incorporated into continuous flow manufacturing systems.

In this paper, we propose that the industrial-scale deposition of zeolite films could be achieved using ultrasonic nozzle spray deposition (UNSD), in which high-frequency standing waves introduced by an ultrasonic nozzle produce uniform sized droplets of cast suspensions at tens to hundreds of micrometers. The droplets are carried by the flow and deposited on a substrate, which results in a uniform thin film following the removal of the solvent [65–67]. Pentacene-containing field-effect transistors prepared using UNSD feature charge mobility 35% higher than that of devices prepared using conventional air spray deposition [68]. UNSD has also been shown to produce thin films of small organic molecules with a more uniform surface topography than that achieved using thermal evaporation deposition [69]. Uniform metal halide perovskite films for photovoltaic devices have also been prepared using UNSD [70]. UNSD enables the efficient use of materials and uniform film coverage on a variety of substrates [71,72]. Nevertheless, the fabrication of pure zeolite thin films *via* UNSD has not been reported.

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This paper reports on the high-throughput deposition of zeolite thin films using UNSD. The proposed method could be incorporated into industrial roll-to-roll processes, thereby opening up new possibilities for the mass production of zeolite films. As a proof-of-concept, we employed UNSD to prepare pure-silica zeolite MFI suspensions on a silicon wafer substrate. We evaluated a range of UNSD operating parameters with regard to their effects on thin film quality. Optical microscopy (OM), scanning electron microscopy (SEM), nanoindentation, atomic force microscopy (AFM), and grazing-incidence wide-angle X-ray scattering (GIWAXS) were used for thin film characterization. Zeolite MFI thin films fabricated using spin-on deposition were prepared as a control sample.

2. Experimental

2.1. Chemicals

Tetraethyl orthosilicate (TEOS, 98%), TWEEN® 80, and tetrapropylammonium hydroxide (TPAOH, 25 wt% in water) were purchased from Sigma Aldrich. Ethanol (99 wt%) was purchased from Merck. The deionized water (DI water) used for the synthesis was purified using the ELGA VEOLIA PURELAB® classic analytical ultrapure water system.

2.2. Synthesis of cast solution containing pure-silica zeolite MFI

We mixed 14.9 g of ethanol with 16.9 g of TPAOH (25 wt% in water) in a perfluoroalkoxy (PFA) container and then stirred it for 10 min. We then added 12.1 g of TEOS to the mixture, at a final molar ratio of TEOS: ethanol: TPAOH: H_2O = 1: 5.6: 0.36: 12.2. The mixture was aged at room temperature for 24 h under agitation. We transferred 6.0 g of the aged solution to a 10-mL sealed glass vial (IntelliVent™ Reaction Vial System) for a hydrothermal reaction conducted in a microwave oven (CEM Discover® Personal Synthesizer with LabMate™ System) at 408 K under pressure of 130–135 psi over a period of 45 min under agitation. A constant reaction temperature was maintained during synthesis by varying the power of microwave radiation between 23 and 30 W. Pure-silica zeolite MFI nanoparticles formed during the hydrothermal reaction. Specific quantities of ethanol and/or TWEEN® 80 may be added to the resulting zeolite MFI suspension to form the cast solution. The cast solutions were stirred at room temperature prior to thin film deposition *via* ultrasonic nozzle spray deposition or spin-on deposition.

2.3. Substrates for thin film deposition

Silicon wafers (p-boron type) with an orientation of (100) ± 0.5° (SUMMIT-TECH Resource Corp) and native oxide were used as the substrate for the deposition of zeolite thin films *via* UNSD or spin-on deposition. The silicon wafers present resistivity of 1.5–100 ohm-cm and a water contact angle of 35°. An entire 6-inch silicon wafer or a small piece of silicon wafer (approximately 2 × 2 cm) was used for thin film deposition.

2.4. Thin film deposition via ultrasonic nozzle spray deposition (UNSD)

In forming cast suspensions for UNSD, the as-synthesized zeolite MFI suspensions were diluted by up to 10 times with ethanol. Surfactant TWEEN® 80 was added to form the cast suspensions with up to 6 wt% of TWEEN® 80. The UNSD device in this study (Model: USD-1515) was purchased from Nano Optical Coating Technology Inc, as illustrated in Fig. 1a. This system is equipped with an ultrasonic atomizer nozzle operating at a frequency of 60 kHz with tunable piezo power between 0.5 and 5.0 W with a default setting of 2 W. Nitrogen was used as the carrier gas at a pressure of 10 psi during the coating process. The nozzle-to-substrate distance was 60 mm, and the injection

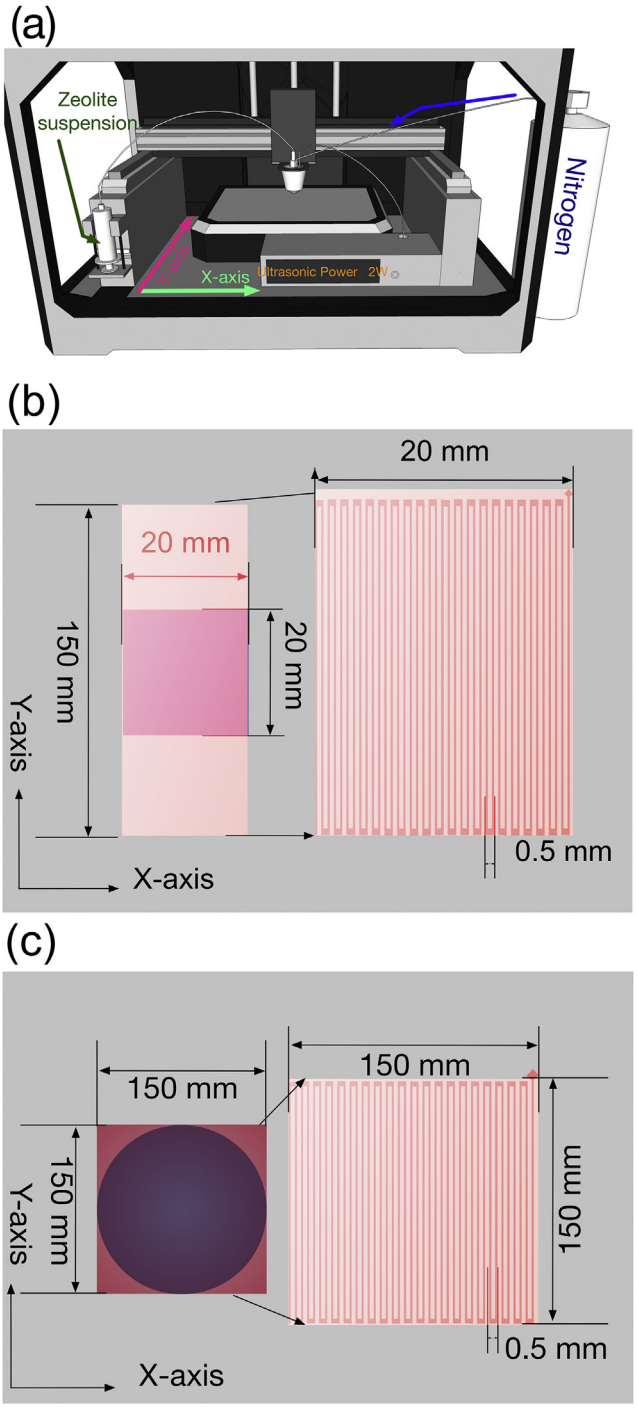

Fig. 1. (a) Schematic illustration of UNSD device; the moving pathway of the ultrasonic nozzle for a (b) small silicon wafer substrate (approximately 2 × 2 cm) and for a (c) 6-inch silicon wafer substrate. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

flow rate of the cast solution was varied between 0.5 and 3 mL/min. The moving pathway of the nozzle across the 2 × 2 cm silicon wafer and 6-inch silicon wafer is respectively illustrated in Fig. 1b and c. The moving speed of the nozzle along the *y*-axis was varied between 50 and 300 mm/s, whereas movement speed along the *x*-axis was maintained at 100 mm/s.

Following UNSD deposition, the coated substrate was transferred to a furnace (pre-heated to 80 °C) to undergo baking at 80 °C for 1 h. The temperature was then increased to 450 °C (at a heating ramp rate of