



Patterning silicalite-1 films using carbon dioxide laser ablation



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ABSTRACT

Nanostructured materials represent an intriguing foundation on which to build new devices for applications in electronics, photonics, energy storage, and biological/chemical analysis. For example, porous, nanostructured materials, such as pure-silica zeolite films, have been used to form 2D and 3D structures for building intricate micro-scale assemblies for light-harvesting, sensing, and microreactor applications. The standard methods used to pattern such devices and features from nanostructured materials are based on either typical microfabrication techniques, which involve either several complex and time-consuming steps, and can result in pore clogging, or the organization of pre-formed seeds/crystals uniformly arranged on the substrate by chemical or physical linkages, which requires precise control and positioning. Here, we present a simple, flexible alternative to both techniques: CO₂ laser ablation. We demonstrate the effects of this technique on a model zeolite thin film system, pure-silica MFI (silicalite-1), to evaluate its potential for patterning complex, multicrystalline, nanostructured materials. We use SEM and XRD to determine the crystallinity, film thickness, surface coverage, crystal size, and crystal habit of the films pre- and post-patterning. Using this technique, we demonstrate that it is possible to make 3D structures in these films, such as channels of varying width (82–611.98 μm), depth (2.58–7.13 μm), separation distance (minimum 25 μm), and edge effects, by varying laser power, spot size, and raster speed. This work introduces a one-step, rapid technique to pattern materials with specific framework structures and subnanometer pore sizes, thus broadening their potential usage in areas that require patterned, micro-scale features.

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1. Introduction

Zeolites and zeolite-like materials have been widely used for gas separation and catalysis due to their unique, three-dimensional, nanoporous, crystalline structure. This structure is enhanced by their ability to host different ions, atoms, molecules and clusters within their channels and cages [1–5]. Increasingly, these nanostructured materials are being suggested as material systems from which small-scale devices, such as microreactors, micro-scale membrane separators, or components for electrical or optical devices, may be fabricated [6–9]. These applications rely on the production of well-controlled zeolite thin films or coatings that are patterned either pre- or post-synthesis to yield an appropriately scaled component or device of interest [10–13]. Based on the specific application of the zeolite films or membranes, the optimum/desired quality and thickness of the final film may vary [14].

Fortuitously, there has been a concomitant advancement in our ability to control the crystal orientation, composition, properties,

morphology and film or membrane thickness of zeolite thin films or coatings. For instance, pre-synthesized zeolite crystals have been used to form closely-packed layers consisting of monograins of zeolite for obtaining specific functionality, and to further form oriented and monodirectional microporous materials [14–17]. Assembled monolayers of zeolites have been made using various types of linkages, such as covalent, ionic, and physical linkages, as well as hydrogen-bonding and micro-contact printing. This has led to the preparation of dense assemblies of zeolite crystals in the nanometer to micrometer crystal size regime with different types of zeolite crystals and on different substrates [15,18–27]. Furthermore, 2D and 3D structures of zeolites with varied geometrical complexity also have been made using techniques like holographic optical tweezers (HOT) and the combination of HOT, microfluidics and colloidal interactions [21,28,29]. Lastly, zeolites have been synthesized, via *in situ* or *ex situ* crystallization, in the form of free standing films as well as films on planar surfaces, spheres, and fibers [30–32].

The advantage of using *in situ* crystallization techniques for the synthesis of zeolite films is that it is a one-step method, forming a monolayer that is transformed into an intergrown, continuous film

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under hydrothermal conditions [33]. This provides the additional benefit of having excellent adhesion of the crystals with the substrate, alleviating the need to prepare seeds. It is well-understood that using zeolite crystals to create dense and controlled monolayers with unidirectional channels is dependent on the ability to make precursor nanocrystals with a narrow size-distribution [16]. This technique acts as a straightforward method to form a high quality monolayer on different substrates. It is unsurprising, then, that zeolite films have been prepared on several substrate families, including metals or metal oxides, like silicon wafers, polished or fused quartz, porous alpha-alumina, and zirconia plates, among others [8,24,34–36].

Historically, the pre- or post-synthetic, one- and two-dimensional patterning of features onto material surfaces has been carried out via lithographic techniques borrowed from the semiconductor industry, such as e-beam lithography, focused-ion beam lithography, proximal-probe patterning, X-ray and extreme-UV ablation, micromolding and self-assembly [7,10,33,37–41]. However, their cost, material specificity, throughput requirements, and limited-scale production have limited their wide-spread adoption to new materials, particularly porous, nanostructured materials. Thus, despite improvements in both synthetic techniques and patterning techniques, patterning large-to-small scale features into nanostructured, porous films, like zeolites and other materials, remains challenging. Moreover, each technique tends to have a limited range of patterning effects, such as size range or edge effects that can be produced for a given material system. This has limited the development and application of porous, nanostructured materials in micro- and nano-scale devices. In order to fully utilize these materials, patterning techniques that are simple, flexible, inexpensive, and broadly applicable to many types of porous, nanostructured materials must be created. To successfully pattern features onto porous, nanostructured materials, these techniques must (1) minimize pore-clogging from deposition of other materials onto the surface, (2) allow the retention of the surrounding materials' porous network and crystallinity, (3) be compatible with potentially high roughness, polycrystalline film materials, (4) be able to pattern at multiple length scales, and (5) be able to selectively “tune” the feature effects, such as edge shape, whether in an x - y plane or in terms of patterning depth. Preferably it should also be a one-step process, without the need for masking or the deposition of a sacrificial patterning material (e.g., photoresist). Although many options are available that meet one or two of the stated constraints, few meet all five [37–40, 42–44]. Of these few, laser patterning, i.e., making patterns or features using laser ablation, represents an intriguing solution to the challenge of patterning porous, nanostructured materials.

Laser ablation has been used for micromachining or etching silicon for over two decades [45,46]. This technique creates 3D patterns, and has the advantage of being a direct writing, one-step method with a resolution limit comparable to other multi-step techniques e.g., projection printing or photolithography [47,48]. Previously, laser ablation via CO_2 , Nd:YAG, and Ar^+ lasers has been used to make micro-holes and other patterns in metals, glass, or silicon substrates, and has been used for the heating and densification of coatings of TiO_2 , SiO_2 , TiO_2 - SiO_2 , Ta_2O_5 and WO_3 [49–53]. The structural and physical effects of laser densification have been studied on tetraethylorthosilicate (TEOS) coatings (dry, porous films with thicknesses in the range of 200–250 nm) on fused silica substrates as sol-gel films where pattern widths of 100–150 μm were obtained using a 1.06 μm line from Nd:YAG laser in indirect-writing mode. Moreover, the damage caused to dielectric coatings/films by laser ablation has also been studied, and it was shown that the resulting laser irradiated regions developed altered optical properties that could be used for storage and device purposes [54].

Of the aforementioned laser ablation techniques available, CO_2 laser ablation is the most widely used. This technique has been

used for various aspects of silicon-based device creation for optical communications, optical fiber-based sensing [55], frequency metrology, and optical coherence tomography [56,57]. CO_2 laser ablation processes typically involve heating the material of interest to the point that the material softens. Due to its point-to-point ablating abilities, intricate and complicated profiles can also be without the need for expensive masks. For instance, CO_2 lasers have been used to achieve variation in the refractive index of photonic crystal fibers by creating long period gratings via the local release of mechanical stress in the fiber when the fiber is irradiated and the temperature of the exposed regions exceeds the glass-transition temperature of the material [58–60]. CO_2 laser processing of sol-gel films has been studied for various applications in optics, including electrochromic films, channels and slab-waveguides [49,51,61,62]. Widespread application of patterned sol-gel films, as optical interconnects, channel waveguides, optical switches, etc. has propelled our study towards the use of CO_2 laser ablation in patterning zeolite and zeolite-like materials. We hypothesize that this could be a simple, flexible, cost-effective, one-step, maskless, and fast process, in comparison to current lithographic techniques.

In order to determine if CO_2 laser ablation on zeolite films could meet the aforementioned patterning requirements, we determine if simple channels or lines, which are commonly fabricated features in optical applications of sol-gel films, could be created via a CO_2 laser-based, serial writing process. In this paper, we explore the idea of creating features in pure-silica zeolite MFI (otherwise known as silicalite-1) films using CO_2 laser ablation as a primary 3D micropatterning tool, analogous to a 2D e-beam lithography machine or projection printing. The fabrication process is based on the heating effect (thermal shock) of focused, high-frequency (100 Hz), continuous CO_2 laser irradiation. The reasoning behind the use of a high-frequency laser, as compared to a low-frequency CO_2 laser, is that the higher frequency provides a higher fluence/laser energy density to the surface of the films, which in turn cause greater release of the internal stress of the film, thus making it a more effective serial writing technique [59]. Therefore, using thin films of the well-understood, pure-silica zeolite MFI (silicalite-1) as a proof of concept zeolite material, we examine the effects of film thickness, laser power and exposure length on the patternability of these films. The rough, polycrystalline films are characterized pre- and post-patterning to determine the impact of the method on their composition and crystallinity.

2. Experimental

2.1. Synthesis of pure-silica (MFI) films

Silicon wafers (100) (University Wafers, 0.008–0.02 Ω -cm, 600–700 μm thick) were used for *in situ* synthesis of pure-silica (MFI) films. They were first washed using Piranha Solution [volume ratio; 1 Hydrogen Peroxide (H_2O_2 , 40 wt%): 4 Sulfuric Acid (H_2SO_4 , 98 wt%)] and drying under N_2 . The reaction gel was prepared by first mixing DI H_2O and Tetrapropylammonium Hydroxide (1.0 M in H_2O , TPAOH, Aldrich) in a plastic container, followed by slowly adding Tetraethylorthosilicate (98%, TEOS, Aldrich) while stirring. Two different molar ratios of the reaction gel were used – 99.0 H_2O : 0.14TPAOH: 0.84TEOS (Scheme 1) and 165 H_2O : 0.32TPAOH: TEOS (Scheme 2). The mixture was aged for 1 h under stirring at room temperature. The two different gel composition used in this work provided different aspect ratios of the silicalite-1 crystals that formed the film (Fig. 3). The synthesis solution was then charged into 23 ml Teflon-lined Parr autoclaves with silicon substrates placed either horizontally or slightly slanted in the liners, with their polished surface facing upwards. Crystallization was carried out at

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