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Impact of deposition and laser densification of Silicalite-1 films on their optical characteristics

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ABSTRACT

Although the field of integrated optics has advanced tremendously in the past two decades, the state-of-the-art still lags behind its electronic counterpart, particularly in the development and integration of new optical materials systems. Nanostructured materials, and in particular, porous, nanostructured materials, often have unique and complex relationships between their structure and their resulting optoelectronic properties. These relationships may be tailored during or after synthesis or deposition, leading to potentially intriguing new material systems suitable for various applications in integrated optics (tunable lasers, waveguides, transmitters, etc.) in the visible or near infrared regions. Zeolites represent a unique example of this material class; with their uniform microporosity and structural symmetry, their physicochemical and optoelectronic properties may be tailored to present a broad range of structures, compositions, surface areas, chemical and thermal stabilities, refractive index, dielectric constants, etc. Here, we synthesize a model zeolite system, silicalite-1 (MFI), in film form and characterize the resulting films both before and after partial laser densification to evaluate its potential for integrated optics. We use scanning electron microscopy, X-ray diffraction, and ellipsometry to determine the crystallinity, film thickness, surface coverage, crystal size, and crystal habit of the MFI films. We explore the fundamental optical properties of these films, such as index of refraction, and absorption and transparency windows, as a function of deposition method and film orientation. Within these parameters, we discuss their potential versatility and how slight structural changes induced via CO_2 laser-assisted densification impact their resulting IR and Raman characteristics. The resulting randomly- and *b*-oriented films of thickness 94.32–510.31 nm showed the ability to reach a range of refractive indices (1.327–1.678), depending on film orientation, deposition technique, and crystallization time. The intensities of their IR (1400–400 cm^{-1}) and relative Raman (1500–600 cm^{-1}) absorption regions indicate an increase in crystallinity with laser irradiation from 10 to 20% power, however, crystallinity then decreases above 30% laser irradiation. These changes are all possible without changes in the overall composition. Determining these fundamental optical properties will allow us to explore the functionality of these materials for a wider array of applications in optics and electronics, where nanostructured materials can make a significant difference in scale, cost, efficiency, and overall performance. The results of this study will help determine the suitability of zeolites for optoelectronic materials, and will broaden their usage in optical computing, signal processing, and a new generation of optical components.

1. Introduction

The high demand for very fast communication and information processing systems has stimulated research towards the study of novel optical materials for integrated optics, specifically those that are compatible with laser-assisted photonic systems/devices, e.g. optical switches, modulators, waveguides, interconnects, couplers, and microlens arrays [1–8]. Nanostructured optical materials have been studied extensively for applications in optoelectronics, including computing, communication, and sensing [9,10]. These materials often have unique optical properties that arise due to either their nanoscale confinement or their nanoscale features, and that are fundamentally different than those of the same material composition at the bulk scale or in an amorphous configuration [11–14]. The use of nanostructured, *porous* materials, like

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zeolites, in these applications further enhances their capabilities, and allows for the addition of guest–host interactions to the capability list [8,15,16]. For example, the presence of one-dimensional pores in microporous, zeolite-like (nanocrystalline, porous materials) materials has been exploited for building highly-ordered, guest–host optical systems [17,18]. It is unsurprising, then, that these materials could be a practical matrix for hosting a number of species, not limited to dye-molecules, resulting in, for example, the generation of zeolite/dye microlasers, where the resulting laser properties are governed by the size, shape, and arrangement of the guest molecules and pores in their microstructure [12,19]. Alternatively, when used as a coating on fiber-optic sensors, the surface area of the sensor and its subsequent interaction with light is substantially increased, thus enhancing the sensitivity of the device by one hundred fold [19,20]. Lastly, the zeolite matrix has the potential to act as a 3D well of dielectric material, which may confine the excitons of its guest semiconductor particles [1,14,21,22].

Zeolites, which are typically synthesized through a sol–gel process, are potentially well-suited as optical materials due to their optical transparency characteristics, post-synthetic modifiable composition, controllable porosities, compositional purity, and doping abilities [23,24]. Additionally, they can be made in a variety of forms, including membranes, films, fibers, fine powders, and monoliths. The ability to control zeolites' film/membrane thickness, along with their 3D crystal arrangement, into a desired, predetermined hierarchy, has pushed the boundaries of their applications beyond their traditional uses as industrial catalyst, separation membranes, ion-exchange networks, etc., to next-generation electronics components, such as insulators, as well as next-generation coatings, such as antimicrobial coatings, corrosion resistant coatings, etc. [2,25,26]. Additionally, the crystalline material structure of these materials possesses greater mechanical strength compared to their nanostructured amorphous counterparts of similar composition, thus increasing their potential for use in a variety of applications that require mechanical strength or durability, such as optical polishing [12,27].

In order to extend the application of these nanostructured, porous materials in optoelectronics and integrated optics, it is necessary to have a detailed understanding of their relevant material properties, e.g. refractive index (RI), absorption, etc., in addition to strict control of these properties [4]. For example, silicalite-1 (MFI) is a commonly-used and well-understood zeolite system, primarily due to its robust and facile synthetic techniques. It has been synthesized by direct hydrothermal or secondary growth in the form of powder, films, and membranes on different substrates [14]. Over the past two decades, scientists have optimized its synthesis, surface characteristics, molar composition, substrate, crystal orientation, and film thickness in order to alter its physicochemical, electronic, and mechanical properties [1,12].

Previous literature on this model zeolite system has shown that silicalite-1 (MFI), when synthesized with high purity and low water content, and in the appropriate form, may be a promising material for optical waveguides [1,27]. Therefore, it is easy to extrapolate that this material system could act as an effective V-type antireflection coating, or as the basis for Bragg stacks or more complex Gradient Refractive Index (GRIN) materials (Fig. 1), which have continuous variations in their RI in the radial, axial or spherical direction and could theoretically be derived from index-modified SiO_2 materials, such as silicalite-1 films [2,24,28–32]. For example, the potential effectiveness of silicalite-1 films as V-type antireflection coatings depends largely on their RI values, with the resulting percentage of reflection at a given wavelength, λ, for a film–substrate system given by Eq. (1), [24].

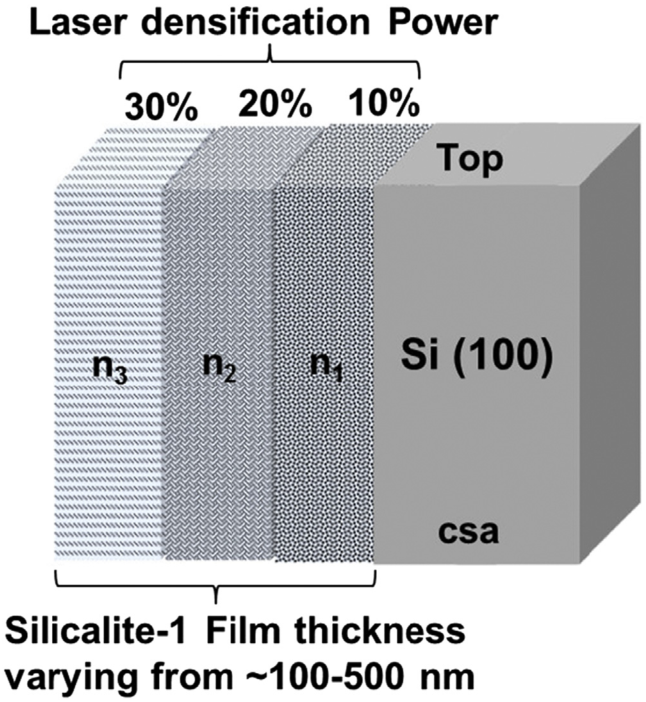

Fig. 1. Cross-sectional (csa) illustration showing formation of different RI regions on silicalite-1 film when irradiated at different laser power (10, 20 and 30%), due to different degree of porosity, densification and ratio of amorphous to crystalline material.

$$R = \left(n_1^2 - n_o n_s\right) / \left(n_1^2 + n_o n_s\right) \tag{1}$$

where, n_1 is the RI of the film (i.e. silicalite-1), n_s is the RI of the substrate (i.e. Si (100)), and n_o is the RI of the medium, commonly air ($n = 1$). This relation requires a detailed understanding of the wavelength-dependent RI of the silicalite-1 material, which could vary based on film deposition method, crystal size, number of defects, etc., all of which must be explored in detail to verify the material's use in this type of application. Moreover, post-synthetic physical processes like ion-exchange, physisorption, adsorption, or densification can impact these properties [2,33]. However, there have not been many attempts to study its optical properties on the basis of the aforementioned optimization or to evaluate this material for its suitability as an optoelectronic material.

In this study, our interest lies in primarily in creating zeolite films with tunable optical properties, such as their RI, either by modulating the processing conditions (e.g. crystallization time) or post-synthetic modifications of selective regions (e.g. CO_2 laser based-densification). CO_2 lasers can be used to densify zeolite films, which have a uniform microstructure that facilitates uniform densification. This causes a density gradient across the film, and minimizes loss due to optical scattering at crystal boundaries, hence altering the film's optical properties as well as its porosity, film thickness, and roughness [34–37]. Here, we explore the model zeolite system, silicalite-1 (MFI)'s optical properties (RI, as well as IR and Raman absorption spectra) and evolution of IR and Raman spectra upon in response to modification to synthetic or deposition parameters. Furthermore, we explore the effect of densification or ablation via CO_2 laser irradiation on these properties. This process could be used to fabricate waveguides and other structures from the materials, and has the potential to convert silicalites-1 into GRIN in less than 30 min using laser assisted densification [34–39]. Moreover, for these applications, laser irradiation could be used as a