Chapter 8: Summary and Conclusions

1. Summary and Conclusions

This thesis is the result of two separate pieces of zeolite science research that address different issues in the development of new synthetic routes to zeolite thin films. Part I of this thesis presents the development of a new route to the synthesis of fluoride-mediated, pure-silica zeolite thin films, with a particular emphasis on the application of these films as low dielectric constant (low-*k*) materials. Past efforts to utilize pure-silica zeolite thin films in applications such as chemical sensors, membrane reactors, and microelectronic devices have been limited by the number of pure-silica zeolite materials that can be accessed via current zeolite thin film synthetic approaches. These approaches include *in situ* crystallization (a process where the zeolite films is grown in situ onto a bare substrate from a dilute precursor solution that is free from preformed crystals), and the spin-on of zeolite nanoparticle suspensions. Of the 19 zeolite topologies with pure-silica compositions, only 4 (structure codes MFI, MEL, *MRE, and BEA*) have been prepared into films for zeolite low-*k* applications. A facile method that could produce films of this type – and therefore extend the library of pure-silica zeolite materials available for use – would be of great use.

Two methods for the synthesis of fluoride-mediated, zeolite thin films were examined to determine if they could overcome the limitations of fluoride-mediated zeolite syntheses, which render them incompatible with standard film synthesis techniques. The first method utilised a seeding and dilution modification to typical *in situ* film syntheses. The second method applied the vapor phase transport method to the zeolite mineralizing agent, fluoride, to crystallize a precursor film deposited by dip-coating techniques. These methods were investigated using fluoride-mediated zeolites with the LTA topology, which is potentially useful as a low-*k* material when synthesized in the pure-silica composition, due to its low framework density. Although the modification of typical *in situ* synthesis procedures by seeding and diluting the zeolite precursor gel resulted in the ability to obtain germanosilicate and silicate zeolites with the LTA topology within a greatly increased composition range, the modification did not yield films of these materials. This was due in part to the degradation of the substrate materials used due to direct contact with the fluoride mineralizing agent. However, using the vapor phase transport of fluoride (VPTF) method, thin films of silicate and germanosilicate zeolites with the LTA topology were obtained on a variety of substrates, which included (100) silicon, glass, and quartz materials. This method also used chemical techniques to modify the surface of the substrates was used to promote good adhesion of the resulting films to the surface of the substrate. The films were characterized by a combination of X-ray diffraction, field emission scanning electron microscopy, X-ray energy dispersive analyses, and mechanical testing via nanoindentation to determine their quality. From these analyses, the films were determined to be polycrystalline, intergrown, continuous, and well-adhered to their substrates. Additionally, the silicate films were determined to have mechanical properties capable of withstanding the chemical-mechanical polishing techniques used in fabrication of microelectronic devices, one of the potential applications for pure-silica zeolite thin film materials.

To evaluate if the vapor phase transport of fluoride method could further expand the library of pure-silica zeolite materials available as thin films, the thin film synthesis of the pure-silica zeolite systems CHA, ITW, STT, and -SVR were attempted using the vapor phase transport of fluoride method. These attempts yielded thin films of each type of material on surface-modified, (100) silicon wafers. Like the pure-silica zeolite LTA thin films, the CHA, STT, ITW, and -SVR films were polycrystalline, intergrown, continuous, and well-adhered to their substrates. The films are characterized by a combination of techniques, including X-ray diffraction and field emission scanning electron microscopy.

As mentioned above, the development of pure-silica zeolite thin films as low dielectric constant (low-*k*) materials is of particular interest to the semiconductor industry. In order to decrease the feature size in integrated, without potentially increasing cross-talk noise and energy dissipation, the industry must develop an ultra-low-*k* (between 2.3 – 2.6) material to replace nonporous silica ($k = 4.0$) as the dielectric film insulating the wiring between transistors. Pure-silica zeolites have *k*-values that are tunable based on the selection of topologies with different porosities, which are functions of their framework density. For instance, the LTA topology has the lowest framework density (FD = 14.2) among all available pure-silica zeolites, and therefore could have the lowest dielectric constant. Additionally, zeolites could be useful as low-*k* materials due to their high mechanical strength, high heat conductivity, high thermal stability, and high chemical stability. For these reasons, the exploration of low-framework density, pure-silica zeolites as low-*k* materials has generated great interest.

The fluoride-mediated, pure-silica LTA, CHA, STT, ITW, and -SVR zeolite powders and films were investigated for low dielectric constant (low-*k*) material applications. The pure-silica ITQ-29 (LTA) films synthesized in Chapter 3 using this method were demonstrated to have a *k*-value of 1.69 via parallel-plate capacitance measurements, which is the lowest value experimentally obtained on any zeolite film. The pure-silica zeolite powders crystallized in conjunction with the film syntheses of these materials were examined via Time Domain Reflectometry at high frequencies to determine their dielectric properties. This investigation demonstrated that these materials were appropriate for low-*k* applications, especially the LTA topology, which has the lowest intrinsic dielectric constant of all the pure-silica zeolites. Consistent with our previous studies, all the zeolites investigated here, except STT, gave *k*-values lower than predicted from their porosities using the Bruggeman effective medium model, which has been commonly used and found valid for correlating dielectric constants of amorphous porous silicas with their porosities. Comparison of the dielectric data to the k-values of other pure-silica zeolites measured using this technique also showed interesting dielectric behavior with respect to porosity. These data demonstrated that the dielectric properties of zeolites are affected by their pore structures, even though they are still primarily a function of porosity. Generally, materials with low framework density *and* high symmetry structures were shown to have low relative permittivities.

Part I of this thesis demonstrates that there is an inherent difference between zeolites and other porous silicas with respect to the relationship between porosity and relative permittivity, and suggests that by using zeolites, the dielectric properties can be tailored based on not only porosity, but also pore architecture. Using this general relationship between the dielectric constant, and the porosity / pore structure of the zeolite, it is possible to tune the final values of the dielectric properties of the materials. Additionally, Part I shows that the vapor phase transport of fluoride is a facile and general method for the synthesis of fluoride-mediated, zeolite thin films, specifically those with the pure-silica composition. Lastly, the techniques demonstrated here could expand the current library of zeolite films available for a variety of applications.

Part II of this thesis focuses on the development of a photolabile structure-directing agent that could be used to promote zeolite crystallization. This technique would enable the removal of the structure-directing agent from within the zeolite pore space via photolysis and extraction, rather than thermal calcination, which can be incompatible with nontraditional zeolite applications that require the synthesis of thin films, membranes, and nanoparticles of various sizes. Additionally, calcination results in the complete destruction of the structure-directing agent, which can be very expensive and therefore cost-prohibitive for use on an industrial scale. A photolysis technique that selectively cleaves the photolabile molecule could allow for the partial recycling of the structure-directing agent, thus reducing overall costs. Towards this end, the development of partially recyclable, photo-cleavable structure-directing agents is investigated using molecules in the 2-nitrobenzyl family of photoactive molecules, which have been used extensively in the organic synthesis of polyfunctional materials, and undergo photolysis via long-wave UV radiation with a Hg arc lamp to generate the unstable 2-nitrosophenyl derivative of the 2-nitrobenzyl photochemical protecting group.

The first photolabile structure-directing agent (designated as P-SDA 1) developed was a derivative of 8,8-dimethyl-2-phenyl-1,4-dioxa-8-azoniaspiro[4,5]decane hydroxide, an acid-cleavable molecule that has been demonstrated to produce the zeolite known as mordenite (structure code MOR). The synthesis of P-SDA 1, 8,8-dimethyl-2-(2-nitrophenyl)-1,4-dioxa-8-azoniaspiro[4.5]decane hydroxide, had not previously been reported in literature, but was synthesized via standard ketalization reaction procedures, where a diol is used to protect the ketone functionality of a molecule, followed by the production of a water molecule. This reaction was followed by quaternization of the amine present, and ion exchange to the final hydroxide form, generating P-SDA 1 in approximately 50% overall yield. Cleavage of the photolytic P-SDA 1 was first demonstrated in a homogeneous solution of acetronitrile, and then demonstrated while intercalated into a dealuminated zeolite with the FAU structure, which is an open-framework zeolite used as a model to evaluate the ability of P-SDA 1 to undergo photolysis while confined within the pore system of a zeolite framework. The structure-directing ability of P-SDA 1 was evaluated via attempts to synthesize silicate and aluminosilicate zeolites through procedures similar to those that result in the crystallization of various compositions of the BEA* and MFI zeolite structures. These syntheses resulted in the formation of primarily amorphous and layered materials. One synthesis did yield crystalline material with the MFI zeolite topology; however, this synthetic result was not reproducible. The inability of this molecule, when compared to its acid-cleavable equivalent that could produce crystalline material with the zeolite structure MOR, to produce a zeolite material was likely due to a combination of factors. These included its larger size, bulkier aromatic group, and changed electrostatic interaction potential due to the presence of the nitro substituent's electron-withdrawing nature when compared to the acid-cleavable equivalent of P-SDA 1. Although this particular molecule did not demonstrate the feasibility of the photolabile structure-directing agent route to zeolite syntheses, it did demonstrate the ability of the 2-nitrobenzyl class of molecules to cleave within a zeolite pore space when the material is in planar conformation. This suggested that this class of molecules could be useful for this route; further investigation of this route was therefore focused on the development of smaller photolabile structure-directing agents.

The second photolabile structure-directing agent (designated P-SDA 2) developed was 1-(2-nitrobenzyl)-1H-imidazole. Imidazole-based structure-directing agents have been used to synthesize a variety of zeolite phases, including zeolites with the ITW, MTT, TON, and MTW topologies, and other novel zeotype structures. The organic molecule was synthesized according to literature procedures via the photochemical protection of the imidazole functionality by the 2-nitrobenzyl photochemical protecting group, which resulted in P-SDA 2 in 30% overall yield. The structure-directing ability of P-SDA 2 was evaluated via synthetic attempts to produce aluminophosphate zeolites, using procedures based on the syntheses of $AlPO_4$-5 (structure code AFI), VPI-5 (structure code VFI), and MAPO-34 (structure code CHA). The aluminophosphate class of zeolites, which crystallizes under acidic conditions, is unusual in that crystallization of these materials can occur in a matter of hours, rather than days, as with aluminosilicate zeolites. In this case, a control molecule, 1-benzyl-1H-imidazole, a non-photoactive molecule designated as SDA 2, was used to screen conditions for the synthesis of aluminophosphate zeolites, resulting in the production of $AlPO_4$-5 (structure code AFI) and $AlPO_4$-36 (structure code ATS). This control molecule was also used to demonstrate the synthesis of MAPO-36 (structure code ATS) under metal-substituted, aluminophosphate synthetic conditions. Attempts to synthesize aluminophosphate zeolites with P-SDA 2 using conditions that produced microporous crystalline material with SDA 2 yielded several unknown, and likely mixed, crystalline phases, although the primary results of these syntheses were dense phases and hydrated phases. The addition of magnesium to the synthesis, using MAPO-34 procedures, also resulted in the synthesis of unidentified crystalline materials. In all of these materials, P-SDA 2 was shown to be intact by ^{13}C cross-polarization magic-angle spinning nuclear magnetic resonance (CPMAS NMR) as well as infrared spectroscopy (IR). Complete photocleavage of P-SDA 2 within the crystalline, aluminophosphate materials was also demonstrated by ^{13}C CPMAS NMR; photolysis was carried out on the as-made crystalline samples deposited in a thin layer via drop-coating techniques onto glass slides. Extraction of the imidazole fragment that was produced by photolysis was carried out via soxhlet extraction.

Overall, the feasibility of the photolabile structure-directing agent route to zeolite synthesis was unfortunately not completely demonstrated. P-SDA 1 was unable to reproducibly promote the crystallization of any stable crystalline phase, likely due to its large size; potentially, it could still be useful as a structure-directing agent using other reactive gel compositions or reaction conditions. P-SDA 2, on the other hand, was very capable of producing crystalline aluminophosphate materials, which were easily reproduced. However, none of the crystalline materials was a known zeolite phase. It is likely that one of the phases crystallized with P-SDA 2 contained a zeolite (probably ATS) combined with an unknown phase; however, repeated syntheses were unable to selectively promote the crystallization of only the ATS phase. Additionally, on calcination, some of the crystalline aluminophosphate material produced with P-SDA 2 was structurally transformed to a known aluminophosphate zeolite phase, ATV; however, this transformation was only seen at high temperatures, which also resulted in the destruction of P-SDA 2. P-SDA 2 was obviously capable of acting in a structure-directing role, even though it did not result of the production of known zeolite materials. It is possible that, under other conditions, P-SDA 2 could produce a known zeolite phase. Lastly, even though neither photolabile structure-directing agent was demonstrated to reproducibly crystallize a known zeolite material, both molecules were shown to be capable of photolysis while confined in a crystalline material. This suggests that this route could still be feasible if the photolabile structure-directing agent is appropriately matched to the synthetic conditions.

2. Future Directions

Micropatterned zeolite films and membranes are potential candidates for use in or development of chemical sensor micro-arrays, nanoreactors, molecular storage, and catalysis. Additionally, the ability to directly manage the spatial zoning of open- and closed-pore zeolites is of intrinsic interest to the design of optical and semiconductor devices. The vapor phase transport of fluoride route to fluoride-mediated, pure-silica zeolite thin films developed here could be useful for a number of applications involving micropatterning. First, given that the method is used to crystallize an amorphous precursor gel adhered to a substrate by various coating techniques, the possibility exists to coat the surface with a micropattern using inkjet technology. When crystallized, this could result in novel, nanostructured materials that could be useful to the development of zeolite-coated cantilever sensors, for example. The ability to precisely control where the zeolite is deposited could be very beneficial. Second, this method could be used to synthesize patterned zeolite films, or more precisely, synthesize micropillars of continuous zeolite crystals, via lithographic techniques. Here, we can envision the use of standard lithography techniques to pattern a silicon substrate with a gold grid, with empty spaces that could be later filled in with a zeolite precursor gel that is then crystallized using the vapor phase transport of fluoride route. The gold grid could then be removed using standard lift-off procedures, resulting in the production of a micro-array of zeolite pillars on a surface. These pillars could then be used to evaluate the mechanical properties of the zeolites via nanoindentation techniques. This would be useful, as the mechanical properties of only a few zeolites have been studied to this point, due in part to the difficulty of producing large enough single crystals to evaluate. Lastly, it could be possible to combine the thin film synthesis techniques developed here with the photolabile structure-directing agent route to zeolite crystallization if the appropriate photoactive organic molecule was found. Some spatial patterning of microporous materials has been done using UV irradiation / ozonolysis and physical masks, but it results in the destruction of the structure-directing agent used to synthesize the zeolite films. Using a photolabile structure-directing agent to generate zeolite thin films would allow patterning and pore functionalization of the zeolite pore space in conjunction with patterning of the zeolite film itself. Overall, the techniques developed here could be very useful for the development of micropatterned zeolite films and membranes.