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Development of etching processes for the micropatterning of silicalite films

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Abstract

Silicalite (SIL-1) polycrystalline films have been synthesized on Si wafers and then micropatterned using both dry (ion milling, reactive ion etching) and wet etching processes after deploying a resin mask on the film top surfaces. The advantages and characteristics of the different etching processes are discussed and related to the orientation of the zeolite crystals in the films. Finally, the etching processes developed can also be used to release freestanding zeolite structures. This is demonstrated for the fabrication of bulk zeolite microcantilevers with a high aspect ratio.

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1. Introduction

The terms micromachining, microfabrication, micromanufacturing and microelectromechanical systems (MEMS) describe the fabrication of devices with at least one of their dimensions in the micrometer range. In the chemical technology field, microfabrication concepts have found relatively few applications to date compared to the microelectronics industry, which is mainly due to the fact that production scenarions in the chemical industry usually involve the processing of high volume feeds, often containing impurities and foreign elements. This is far from the clean room environment typical of the electronics industry, and presents obvious challenges for processing in constricted spaces. In spite of this, several important developments in the realm of microdevices for the chemical and process industries have taken place during the last 15 years, mainly in the fields of microreactors and sensors.

Microreactors offer potential advantages from the point of view of design and operation of chemical processes [1–4]. The improved heat and mass transfer properties typical of microfluidic systems enable the use of more intensive reaction conditions that result in higher yields compared to those obtained with conventional size reactors and allow other desirable characteristics (e.g. increased safety). Microfabricated components already include valves, static mixers, heat exchangers and reaction channels on integrated devices. As a consequence, the *lab-on-a-chip* concept has emerged, representing the goal of miniaturizing chemical, biological, and biomechanical analyses [5], as a scaled-down analog of a chemical processing plant in which a drastic reduction of reactants, and energy consumption and considerably lower processing times can be achieved. Similarly, the field of gas sensors has undergone a tremendous shift towards miniaturization in recent years, driven in part by the need to develop sensor arrays for the analysis of specific components in complex mixtures (aromas, explosives, and pollutants), e.g., in the so-called *electronic nose* devices [6]. Research efforts in this area have been directed not only towards developing sensors with a higher sensitivity, but especially, to increasing the selectivity of analysis by implementing molecular recognition functions.

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While many of the precision engineering techniques developed for the electronics industry can be used in the miniaturization of chemical systems [7], the different requirements lead to the use of different materials and specifications. Thus, whereas finer line widths and standardized materials are key demands in the integrated circuit industry, miniaturization in chemical and process technology applications frequently emphasizes features such as high aspect ratios, special properties (catalytic, adsorptive) and materials resistant to process conditions. It is often the case that the materials amenable to standardized processing (e.g., silicon, silicon carbide, aluminum) are different from those that enable novel functionality [8]. This has led to the use of alternative substrates (e.g., polymer-based materials) to replace the commonly used glass and silica wafers [3].

Zeolites constitute a family of highly interesting technological materials, on account of their framework structure, with pores of subnanometric size, and their remarkable properties in catalysis and adsorption [9,10]. In particular, the possibility of hosting different ions, atoms, molecules and clusters in the zeolite structures has opened up numerous opportunities as nanomaterials with advanced properties [11,12]. During the last two decades, procedures for the preparation of zeolite coatings as films and membranes on different supports have been developed, opening up new applications in the fields of reaction and separation as shown by several reviews in recent years, e.g., [13–15]. Among the novel applications, the deployment of zeolite films seems highly interesting for microchemical systems [16] (microreactors and membrane microseparators). Also, the molecular recognition functionality of zeolites has been used in chemical sensors, where zeolite coatings have been shown to greatly increase the selectivity of reactive [17] and mass sensing devices [18].

Given the interesting properties of zeolite coatings, a significant effort has been carried out to combine the experience gathered in growing zeolite films and the fabrication methods used in the electronic industry to prepare microstructured supports, especially on Si substrates. Several works in the mid 1990s [19–21] explored the formation of zeolite films on Si wafers and the possibilities to control crystal orientation. These methods have been expanded and adapted in recent years to produce catalytic zeolite coatings on microchannels and zeolite micromembranes, for use in microreactors and microseparators [22–26]. Recently, we have reported the formation of continuous zeolite films on microstructured supports yielding unprecedented fluid–solid contact area [27].

The above works have been focused on the development of homogeneous zeolite films for the applications envisioned. However, other authors have developed different approaches targeted at creating patterned zeolite coatings rather than homogeneous films. Notably the group of Yoon [28] has developed methods to create 2D and 3D patterns on different supports that employ zeolite microcrystals as building blocks using different techniques (covalent bonding, ionic bonding, and adsorption), that enable different applications [29]. The procedure usually involves creating a pattern of functional groups on the desired surface using photopatterning [30], or microcontact printing [28], then exposing the patterned surfaces to a suspension of crystals that become tethered on the surface. Other authors [31] obtained patterned films with significant intergrowth by immersing a gold-patterned surface into a synthesis solution, and taking advantage of the weak adhesion between zeolite crystals and gold surfaces.

Here, we propose a different approach to the creation of patterned zeolite coatings on Si supports. Instead of preparing zeolite crystals and attaching them to the desired supports following a certain pattern, we have first created a continuous zeolite film on the support, then developed a pattern on it by using etching procedures similar to those used in microfabrication. This route allows a direct control on the thickness and degree of intergrowth of the zeolite film, but makes it necessary to modify patterning methods to adapt them to the particular characteristics of zeolite films. In this work, SIL-1 films have been synthesized on Si wafers and used as structural layers for micropatterning using physical (ion milling) and reactive (reactive ion etching) dry etchings as well as wet etching processes. To our knowledge, this is the first work where these etching techniques have been applied to “c” and “b” oriented polycrystalline zeolite films. The results obtained provide useful information from a fundamental point of view of the etching process itself when applied to polycrystalline films, and allow to estimate the different etching rates over “c” and “b” oriented SIL-1 microstructures before and after template removal. Finally, the techniques developed can also be used to release freestanding zeolite structures, e.g., for the fabrication of bulk SIL-1 microcantilevers.

2. Experimental

2.1. Preparation of “c” oriented SIL-1 layers over Si wafers 3″ in diameter

2.1.2. Preparation of nanosized SIL-1 crystals

Colloidal silicalite to be used as zeolite seeds was prepared by a hydrothermal route using a solution with the following composition $408H_2O:25TEOS:9TPAOH$ (where TPAOH stands for tetrapropylammonium hydroxide and TEOS for tetra-ethyl-orthosilicate) according to the recipe of Mintova and Bein [32]. First, a mixture of 4.62 g of TPAOH 1 M and 37.27 g of H_2O was vigorously stirred at room temperature until a clear, homogeneous solution was obtained. 8.09 g of TEOS were then added to solution and stirred for 24 h at room temperature. Finally, the resulting solution was transferred into a 60 ml polypropylene bottle and heated at 100 °C during 20–26 h until a white solution of nanosized particles (80–90 nm in size) was obtained. The resulting product was thoroughly washed with distilled water until pH <8 by repeated cycles of dispersion by ultrasonication and separation by centrifugation at 9000 rpm. Finally, the seeding suspensions were

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