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Oriented assembly and nanofabrication of zeolite A monolayers

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ABSTRACT

A facile and efficient method in order to assemble zeolites for the purpose of generating zeolite nano-micropatterns on the Si wafer was investigated by using e-beam lithography. A monolayer of organized, fully covered and strongly bound zeolite A nanocrystals were formed on the Si wafer substrates without using any chemical linkers. The limits of forming nano sized zeolite A patterns on the Si wafer was tested and it was observed that zeolite A nanocrystals could be assembled on the Si wafers with high precision. The limit of the pattern resolution was defined by the size of the zeolite nanocrystal, which was around 250 nm in the current study. Furthermore, mono and double layers of zeolite A nanocrystals were generated without using any chemical linkers on the substrates for the first time.

1. Introduction

Integrating nano-microparticles as well as biomolecules onto different compounds and forming ordered crystalline films are of great interest for multipurpose systems in the area of electronics, optoelectronics, sensor, and biomedical applications [1–6]. Controlling the position of these elements on the finalized system is crucial so that the integrated system will serve for its designed purpose. The real challenge is to assemble nanoelements, which have many useful properties by themselves, into different compounds for manufacturing advanced materials. The structural order with a broad range of diversity, which exists in those nanoelements can be hypothesized to bring multi-functionality and enhanced selectivity to the manufactured device.

Zeolites are still of great interest due to their large surface area, tunable surface properties, thermal/mechanical stabilities with the above mentioned structural order in the nanometer range. Furthermore they show great promise to immobilize biological molecules and potential use in biosensor systems [7–12]. This is due to several factors that are readily found in zeolites. The number of surface hydroxyl groups, which are important for immobilization applications, can be controlled by applying different heat treatment procedures. Consequently, this may result in altering number of defect sites [13,14]. Accordingly, the critical factors of interest which makes zeolites appealing for advanced applications can be summarized as the sufficient number of surface functional groups ready for further modifications, controllable surface hydrophobic and hydrophilic properties, adjustable surface charge, high dispersibility in aqueous and organic solutions, and promising zeolite-biological molecular interactions [15].

In order to make zeolites serve for such advanced components, it is necessary to ensure that they work in harmony with other elements of the system. Although zeolites can be synthesized in a very broad range of surface characteristics and morphologies, which is important for further zeolite dependant applications; the fact that the synthesized zeolites are in powder form restricts their use in such advanced applications. Thus, it is of increasing interest to organize zeolites in a monolayer on different types of substrates [16–29]. Most of the work for that purpose has been conducted using glass substrates [24–28] in addition with some work on polymeric substrates [18,29]. The most commonly used method is to use molecular linkers in order to form uniformly aligned and closely packed layers of pre-synthesized zeolites on different substrates. However, the research in order to form well-ordered, fully covered, and strongly bound pre-synthesized zeolites on semi-conductive substrates, especially on Si wafers, is very limited [30–32].

Studies conducted on (semi)conductive substrates can be important for further device applications incorporating zeolite and zeo-type materials. Furthermore, the development of new methods of pattern generation on a sub-micron scale is a challenging problem for such applications as well [33]. During the generation of zeolite patterns on different substrates, difficulties can be faced due to the sensitivity of these chemical linkers to humidity. Most linkers need to be mixed with dry solvents like toluene, which tend to dissolve the resist used for the generation of patterns in methods like e-beam (EB) lithography. On the other hand, other patterning methods, such as transfer printing and photo lithographic process that do not necessitate using molecular linkages, are limited to micrometer scale [17,34]. However, fabrication of smaller sizes needs to be developed which integrates pre-synthe-

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sized nanomaterials, in order to meet the demands for high-throughput screening and decreased sample amount [2]. Maximizing the number of assembly sites for biomolecules, and increasing the surface area within the patterns is important for rapid evaluation of biomolecules. Furthermore, a simple and reproducible way, that does not only increase the surface area, but also leads to different activities within each pattern results in controlled selectivities for different molecules with a possible reduction in the overall array [5]. Thus, a practical method that does not require the use of chemical linkers in order to form nano-micron patterns of organized and uniformly oriented mono and multi layers of zeolite nanocrystals with high degrees of coverage on Si wafers should be of great interest.

In the present communication, the focus was on investigating a facile and efficient method in order to assemble zeolites for the purpose of generating zeolite nano-micropatterns on the Si wafer. For that purpose, we report a novel approach, which combines the "direct attachment" method developed by Yoon et al. [28] and EB lithography technique for the purpose of assembling zeolite nanocrystals on the Si wafer. Furthermore, the size limits for the generated zeolite patterns by EB lithography were also investigated.

2. Experimental

2.1. Materials and substrates

Zeolites were synthesized from a mixture having the following chemical composition: $11.25SiO_2:1.8Al_2O_3:13.4(TMA)_2O:0.6Na_2O:700H_2O$, according to the previously reported procedure [35]. Tetraethylorthosilicate (TEOS, 95% Acros) was used as the silica source. The resulting solid particles were centrifuged at 13,000 rpm, washed with deionized water and dried at 80 °C. NANO950 poly(methyl methacrylate) (PMMA) C7 (average MW = 950,000, 7% in chlorobenzene) was purchased from MicroChem (Newton, MA, USA) and used as e-beam resists. Methyl isobutyl ketone (MIBK)/Isopropanol (IPA) (1:2 (v/v)) was used as a developer for e-beam (EB) lithography. Ultrapure water (>18 MΩ), obtained using a MES UltraPure water system, was used for all substrate cleaning steps. P-type Si (0 0 1) wafers were subjected to thorough cleaning without removing the native oxide layer prior to use. After each step, the wafers were blow died with dry N_2 gas.

2.2. Assembly of zeolites

For spin coating experiments, zeolite suspensions of 3 wt% in IPA was used. The zeolite suspensions in IPA were applied to the substrates and spun with 1500 rpm for 40 s. and dried in a furnace at 100 °C for 5 min. These steps were repeated for three times. For ultrasound aided agitation experiments, zeolite suspensions of 3 wt% in toluene were prepared in glass tubes and agitated until they became homogeneously dispersed. Si substrates were dipped into the zeolite suspensions in toluene and ultra-sonicated using an ultrasonic bath for 10 min. Then the substrates were rinsed in acetone and dried using N_2 gas. The methodology for direct attachment experiments was based on the literature report [28]. Si wafers were cut into 2 cm × 2 cm pieces and placed on a clean paper. About 2 mg of zeolite powder was put onto the substrates. Then they were pressed and rubbed onto the surface using a finger. Finally, the zeolite assembled Si wafer substrates were heat treated at 100 °C in a conventional oven for 30 min.

2.3. Formation of zeolite micron-nano patterns

Various concentrations of PMMA were obtained by diluting PMMA C7 with chlorobenzene. 5 wt% and 7 wt% of PMMA were spun on Si wafers with 6000 rpm forming ~400 nm and ~850 nm thick resist films respectively. After coating the resist, substrates were pre-baked for 30 min at 160 °C. Patterns were defined by utilizing EBL system (Xenos XeDraw2 Pattern generator attached CamScan CS3000 SEM). Patterned substrates were developed in MIBK/IPA solution for 60 s, rinsed in IPA, washed in flowing pure water, and finally dried with N_2 gas. All zeolite attachment methods were applied to the PMMA coated Si wafers. The prepared thin films were put into an oven at 100 °C for 30 min. Then the substrates were rinsed and ultrasonicated in acetone and dried using N_2 gas. Degree of coverage was simply judged from SEM results. The binding strength was measured from the remaining zeolite particles on the Si wafers after ultra-sonication for 30 s to 5 min in dry toluene [18,29,36].

2.4. Characterization

X-Ray diffraction measurements were preformed on a Rigaku Ultima 4 diffractometer using Cu Kα radiation. The morphology of the synthesized zeolite nanoparticles and the zeolite thin films on Si wafers were investigated by FEI Quanta 400F field emission scanning electron microscope, operated at 30 kV. For FE-SEM observations, the samples were not coated. AFM measurements were conducted using Veeco Multimode V with Nanoscope V controller. Images were collected using tapping mode.

3. Results and discussions

Zeolite A nanocrystals were synthesized according to the previously reported results using the tetramethylammonium silicate as the silicon source [35]. The most efficient method for zeolite assembly on the Si wafers was tested using the three well established techniques, which are spin coating [31], ultrasound aided agitation [27], and direct attachment methods [28]. The efficiency criteria for the successful assembly of zeolite nanocrystals on the Si wafers were taken as full degree of coverage, strong binding, and organized assembly of zeolite particles with the ability to control zeolite patterns in the nanometer range. Organized assembly refers to having uniformly oriented and fully covered monolayers of zeolite nanocrystals.

Spin coating and ultrasound aided agitation methods did not lead to very organized monolayers. Spin coating the zeolites lead to more agglomerations and low surface coverage with respect to the ultrasound aided agitation method (results not shown). The binding strength can be important for the use of the zeolite assembled substrates in real application areas, since these surfaces might be kept in different chemical/biological solutions and sonicated for immobilization purposes. In the current study, it can be inferred that the zeolite crystals are only weakly bound to the surfaces upon the application of spin coating method, since most of the crystals fell of rapidly from the substrates. It was observed that ultrasound aided agitation method enhanced the formation of zeolite A monolayer. Furthermore, the agglomerated crystals on the very top layer before sonication fell off, and only the first layer bound onto the substrate was left after the sonication. Thus, although the number of crystals decreased up to 60% after 5 s sonication from the overall substrate surface, the percent coverage in the first monolayer was observed to decrease up to 30–45%. Special care should be taken during the application of this method to clean the Si wafer surfaces, which might improve the binding strength.

Direct attachment method developed by Yoon et al. for glass substrates and micron sized zeolite crystals was investigated to improve the zeolite A nanocrystal assembly on Si wafer substrates as an alternative approach [28]. Fig. 1 shows the SEM images comparing zeolite attachment results on the Si wafers after applying