Miniaturizing catalytic reaction on patterned catalyst islands

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Very uniformly distributed Ni/MgO catalyst islands patterned on a silicon substrate were obtained using the microcontact printing (μCP) technique. The catalyst precursor solution contained the component metal nitrates, citric acid, water and 2-propanol. The size, thickness and composition of the catalyst islands are tunable and controllable. The carbon deposition reaction was conducted on the patterned catalyst islands. This μCP technique is flexible to pattern catalyst islands with and without supports.

KEY WORDS: microcontact printing; patterned catalyst islands; carbon deposition reaction

1. Introduction

It has been a great challenge for scientists to be able to control many processes, such as device fabrication and chemical crystallization and reaction, at the micro- or nano-size scale. One of our particular interests is heterogeneous catalysis, which has proved to be a very complicated process to characterize and control, especially under high temperatures and high pressures, because of the heterogeneity in surface structures of catalysts, their changeability with reaction conditions, and the short-lived intermediate species produced in the reaction processes, etc. In last two decades, single crystals of transition metals have been used as model catalysts to characterize some catalytic reactions. Usually the single crystals were reacted with reaction gases, then their surface structures and/or the adsorbate species on the surface were characterized under UHV using a variety of surface analysis techniques [1,2]. Because of the relative simplicity of the surface structures of the single crystals, the research has become easier. However, for most industrial catalytic reactions, the active components usually are deposited and highly dispersed on catalyst supports [3]. The model catalysts of single metal crystals cannot fully reflect the truth and complexity of these catalytic reactions.

Another promising approach to characterize the heterogeneous catalytic reactions is to use catalyst islands patterned within defined regions on substrates as the model catalyst. These catalyst islands are separate with equal distance and are formed with a high degree of similarity in composition, shape and size. Reasonably it is expected that the study should become simpler when the catalytic processes are conducted on the assembly of these single catalyst islands, or just on a single catalyst island. Some *in situ* and microstructure analyzing techniques can be applied to the study. The smaller the catalyst islands, the more homogeneous the catalyst islands should be. Theoretically, it is possible to fabricate single catalyst islands that contain only a few, or even one active site.

Depending on the reaction conditions a variety of carbon products can be formed from reactions involving carbon-containing precursors, including single- and multi-walled carbon nanotubes, carbon fibres, amorphous carbon, carbon nanopolyhedra, and fullererene molecules, and each type of carbon can even have different conformations, density and purity [4]. They can be characterized using a variety of techniques such as TEM, Raman spectroscopy, SEM, XRD, etc., so the carbon deposition reaction is a suitable model catalytic reaction to study the relationship between the nature of the catalysts and the reaction products. In recent years, there has been some progress in the synthesis of carbon nanotubes on patterned catalysts for application in field emission and electronic devices. The techniques applied to pattern catalysts include electron-beam lithography [3,5,6], micromolding in capillaries (MIMIC) [7] and solvent-assisted micromolding (SAMIM) [8], etc. But most of these studies are only capable of forming metallic catalyst islands without catalyst support.

It is known that self-assembly, a common phenomenon in biological processes, can aggregate and organize subunits such as molecules into a stable structure with the lowest energy. Recently it was reported that some unique structures, such as nanosized single-wall nanotubes of MoS_2 [9] and carbon (SWNT) [10] and nanobelts of semiconducting oxides SnO_2, ZnO, CdO, and In_2O_3 [11], have been obtained through controlled thermal evaporation and a self-assembly process. Based on self-assembled monolayers, the microcontact printing (μCP) technique has been developed into a powerful measure to fabricate some unusual structures in micrometer and nanometer scale [12,13]. Using this technique Aizenberg

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et al. [14] got very precisely controlled growth of calcite single crystals. In one previous study [15] we demonstrated that ordered 2D arrays of magnetic nanoparticles of Co, Ni and α-Fe on silicon substrate could be obtained using patterned monolayers as templates. In this report, we use the μCP method to pattern catalyst islands on a silicon substrate, each island consisting of catalyst support MgO and active component nickel. The carbon deposition reaction from acetylene gas has been used as a test reaction.

2. Experimental

Chemicals and substrate: toluene, octadecyltrichlorosilane (OTS), 2-propanol and nitrates such as $Mg(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were obtained from Aldrich and used as received. Silicon wafers were obtained from MEMC Electronic Materials (100 orientation, B doped).

In micro-contact printing, two types of elastomeric PDMS (polydimethylsiloxane) stamps were selected. The first one possesses a structure consisting of an array of parallel lines that are 5 μm in width and 5 μm in separated distance ($5\,\mu m \times 5\,\mu m$), and the second one is $10\,\mu m \times 10\,\mu m$ in structure. The OTS solution (0.2 wt% in toluene) was used as ink. The silicon wafers were first treated with a piranha solution, a 7:3 (v/v) mixture of 98% H_2SO_4 and 30% H_2O_2, at 80–90 °C for 40 min. The micro-contact printing was done following the procedures described in the literature [15] to produce square grids of hydrophobic features on the silicon wafer, then the silicon wafers were immediately immersed into the catalyst precursor solutions which contained 0.1 M of each component of $Mg(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ and citric acid in 1:1 v/v mixture solvent of water and 2-propanol. The silicon wafer was slowly withdrawn from the solution to form many small selected wetting squares on the hydrophilic, bare region separated by the hydrophobic lines (the monolayers of OTS).

The Si wafers patterned with a catalyst precursor were put into a quartz tube fixed in a tube furnace and heated at 350 and 700 °C for 1 h, respectively, then the hydrogen gas was introduced and the temperature was kept at 700 °C for 1 h. The heating at 350 °C is to avoid an explosive decomposition of the citrates that may cause the catalyst component to spread outside of the defined region. The carbon deposition reaction was carried out by changing the H_2 gas to a mixture of 10% C_2H_2 in argon gas at 600 °C. The flow rate is 15 ml/min. After 30 min of reaction, the feedstock gas was changed back to H_2 gas and the furnace was cooled to room temperature.

The microstructure and the morphology of patterned catalysts and carbon products were observed employing a JEM-100CX transmission electron microscope (TEM) with a high voltage of 100 kV, and an XL-FEG scanning electron microscope (SEM). The TEM sample was prepared by putting the carbon deposited sample in a glass vial with 2-propanol solution and was sonicated for 1 h, then the 2-propanol solution was collected and dropped on Cu grids and dried in air. The thickness of the catalyst islands was measured using a Dimension^{TM} 3000 atomic force microscope (AFM, Digital Instruments, Santa Barbara, California) in a tapping mode. The micro-Raman spectra were measured with a Renishaw System 2000 at room temperature in a backscattering mode and with a laser beam of 514 nm; a 50× objective mode was employed, giving an illuminated spot of about 2 μm in diameter.

3. Results and discussion

The formation of a patterned catalyst on the silicon substrate is strongly dependent on the extent of selective wetting of the hydrophilic regions that have been separated by the hydrophobic regions with adsorbed OTS molecules. We found that using an aqueous solution of the catalyst precursor could not lead to the formation of catalyst patterns on the silicon wafer. When the printed wafer was withdrawn from the aqueous solution of the catalyst precursor, the liquid thin film was broken and shrank quickly, and almost nothing was left on the silicon surface. Probably this is because the surface tension in water ($\gamma = 73.8$ dyn/cm) was so strong that almost all the liquid in the formed film shrank into big droplets in a short time, and on the other hand, the affinity between the hydrophilic region and the aqueous liquid film was also not large enough to keep the adsorbed solution. We tried to add citric acid and 2-propanol into the solution to lower the surface tension of the solution and increase their wetting ability with the hydrophilic areas on the Si substrate. We know that the surface tension of 2-propanol ($\gamma = 21.7$ dyn/cm) is much lower than that of the water. This measure did improve the formation of liquid droplets on the hydrophilic regions. In our experiments, we found a uniform liquid film was formed on the patterned Si substrate, and the liquid film was broken and shrank into small liquid drops slowly. However, a new problem was created. Because magnesium nitrate is only slightly dissolved in 2-propanol, when the concentration exceeds 0.1 M the solution easily becomes turbid. So in our experiments we usually limited the concentration to not more than 0.1 M, and each time the solution was used within 1 h after being prepared. In addition to decreasing the surface tension and the wetting ability of the solution with the hydrophilic regions on the Si substrate, the citric acid can form complexes with the metal ions, especially with Ni^{2+}, so citric acid can enhance the stability of the solution, and, furthermore, it has been proved to be an effective approach to improving the homogeneity of the catalysts [16,17].

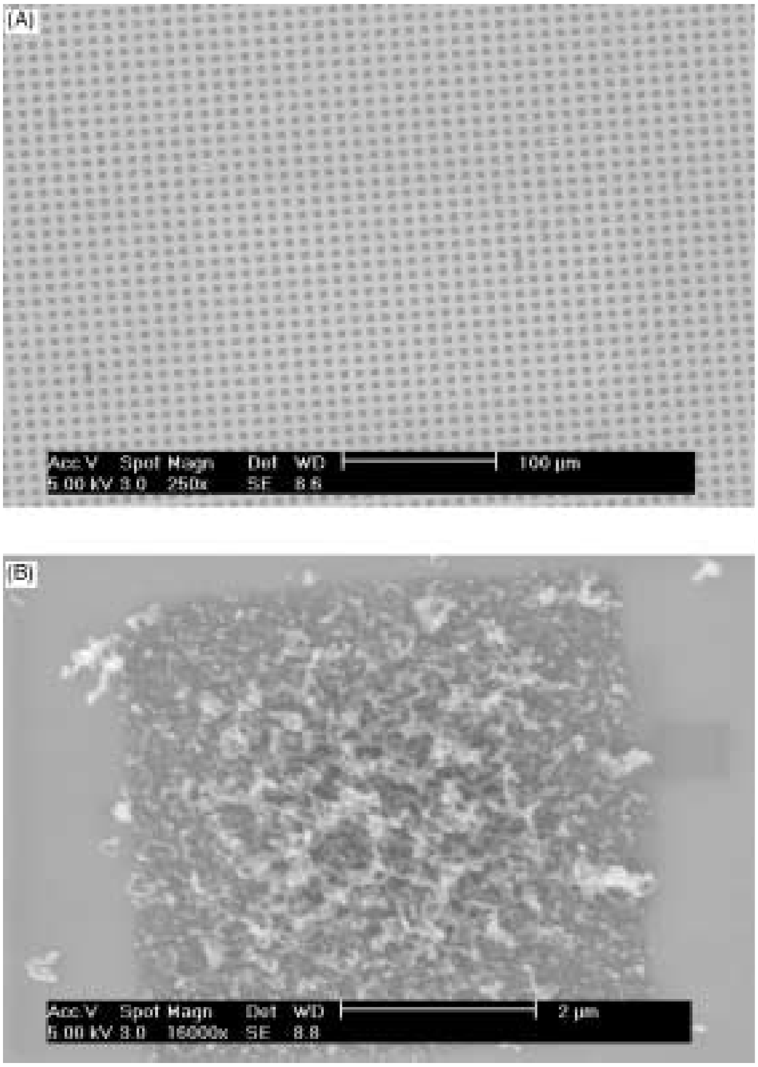

Figure 1. (A) SEM image of patterned catalyst islands with carbon deposit using a $5\,\mu m \times 5\,\mu m$ stamp; (B) magnification of (A) for one catalyst island.

Figure 1(A) shows the patterned catalyst islands deposited with carbon. The catalyst islands are square in shape and are formed very uniformly. In fact it is easy to pattern an area as large as 1 to $2\,cm^2$. Very interestingly it is observed that each catalyst island (figure 1(B)) covered with carbon nanocoils occupies an area of $5\,\mu m \times 5\,\mu m$, which is exactly the same area of each hydrophilic region on the silicon wafer after printing. Obviously in the experiment the formed liquid film in each hydrophilic region did not completely shrink into a droplet as observed in our previous experiment. Probably this is because of the high wetting ability of the catalyst precursor solution that we used.

The surface tension and wetting ability of the catalyst precursor solution can be tunable *via* the controlled addition of citric acid. At low concentration of citric acid, the surface tension is large, and when the patterned silicon is withdrawn from the solution, a thin liquid film with a thickness about the length of the carbon chains of OTS molecules can be formed on each hydrophilic region. After withdrawn out, the liquid film could shrink into many small droplets at the corner of each patterned hydrophilic areas as observed in the previous study [15]. With increase of citric acid, the *wetting ability* of the solution will be increased, which leads to the formation of liquid thin films with a thickness higher than that of the patterned hydrophilic regions. In this case the dried liquid patterns will develop into separate catalyst islands with the exact size of the printed hydrophobic square regions, as observed in figure 1(A) and (B). At high concentrations of citric acid, the liquid film on each hydrophilic area can further develop to be connected to each other to form a thick liquid layer on the whole silicon wafer. After drying we did observe a layer of catalyst thin film with many cracks for Ni on the silicon wafer when the citric acid concentration was very high. So in addition to changing the concentration of the nitrate salt [15] to control particle size, adjusting the citric acid concentration will be an effective approach to control the thickness of the catalyst islands.

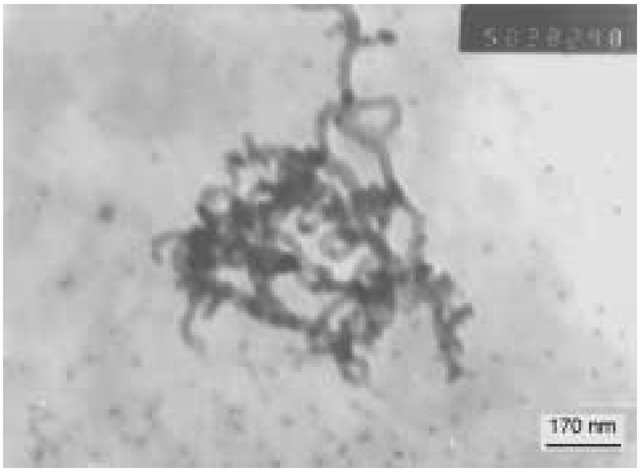

Figure 2. TEM image of carbon deposit on patterned catalyst.

We once used the $10\,\mu\text{m} \times 10\,\mu\text{m}$ stamp to pattern catalysts and bigger catalyst islands were obtained (the picture is not shown here).

Figure 2 shows a TEM image of the carbon deposit on patterned catalyst islands. All of the carbon deposits are carbon nanocoils 30–40 nm in diameter. No hollow channels can be observed in all the carbon deposits. The formation of the carbon products depends on the composition and structure of the catalysts and on the reaction gases. It should not be difficult to get different carbon products by varying the above experimental conditions.

Figure 3 shows an AFM image of a catalyst with a carbon deposit on it. It is found that the thickness of the catalyst islands is about 60–70 nm, while the height in middle of the catalyst islands with a thicker carbon deposit is about 400–960 nm. Clearly, according to our experimental observation and previous study [15], the catalyst island is not flat on the surface. In the drying process, with the evaporation of the solution, the solution will flow to the center of the wetted hydrophilic regions, which will lead to formation of a structure with a thicker center.

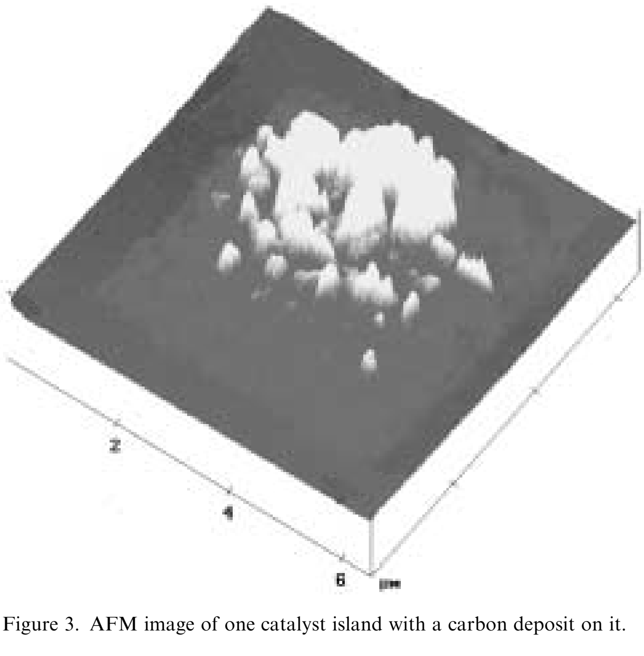

Figure 3. AFM image of one catalyst island with a carbon deposit on it.

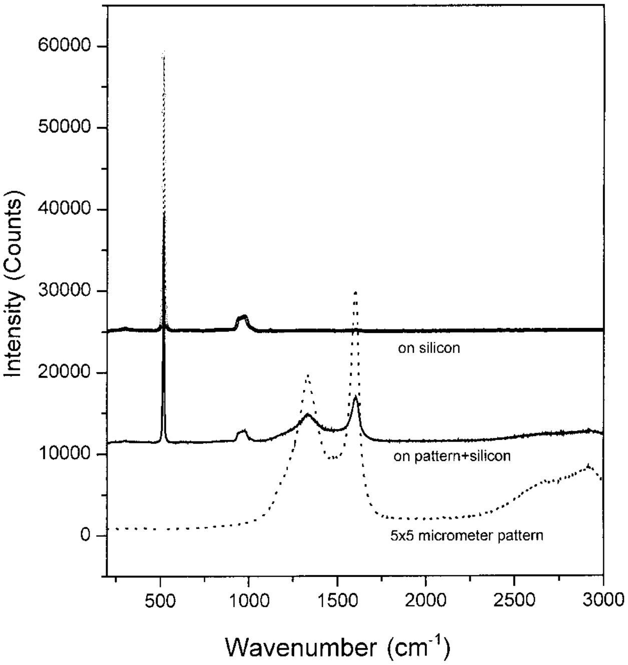

Figure 4. Micro-Raman spectra where the laser spot was focused on a patterned catalyst island with a carbon deposit (bottom), on the boundary of the catalyst island and the silicon wafer (middle), and on the void silicon region between the two catalyst islands, respectively.

Figure 4 shows the micro-Raman spectra. Two bands are observed at $1336\,\text{cm}^{-1}$ and $1602\,\text{cm}^{-1}$ in the bottom spectrum that was obtained by focusing the laser spot on a catalyst island. The band at $1336\,\text{cm}^{-1}$ is disorder-induced in carbon and is called the D line, whereas the $1602\,\text{cm}^{-1}$ band known as the G line is related to crystallized carbon [18,19]. The existence of an intense G line indicates that the carbon deposit is well crystallized, though some amorphous carbon and/or some defects may exist on/in the carbon nanocoils according to the existence of the D line.

The observation of the Raman shifts of the carbon is strictly limited on the catalyst islands. Out of the catalyst islands, only Raman scattering from the Si wafer can be observed (figure 4, top line). When the laser spot was focused on the boundary of the catalyst island and the bare region of the silicon wafer, a weakened Raman scattering reflecting the features of both carbon nanocoils and silicon wafer is observed (figure 4, middle line). Though from figure 1(B), we can find a few carbon nanocoils on the bare areas of silicon wafer between two catalyst islands, we believe these few carbon nanocoils were blown out from the catalyst islands by reaction gas during the reaction. So this approach is a very "accurate and clean" method that can strictly construct the catalyst islands on well-defined regions.

Kind and his coworkers [20,21] directly used the Fe(III)-containing gel-like catalyst precursor as the "ink". After the printing, the catalyst precursor was transferred from the stamp to the substrate. In this way, very long catalyst "stripes" were obtained. By electron-beam lithography [5,6], some metal catalyst "islands" were also obtained. It seems that our method is more flexible in controlling the size and shape of the patterned catalyst islands. More importantly, in our method, not only the metal active component but also the catalyst support, such as MgO, can be simultaneously transferred out from the catalyst precursor solution and printed into the catalyst islands on a large area.

In summary, we demonstrated in this study that patterned catalyst "islands" could be easily fabricated on a silicon wafer. The size, composition and thickness of the catalyst islands are tunable by changing the feature size on the stamp and the concentrations of the precursor solution and citric acid. Carbon nanocoils with a diameter of 30–40 nm were obtained from the carbon deposition reaction using 10 vol% acetylene in argon gas on the patterned catalyst islands. We believe this method can be extended to other catalyst systems for preparing various patterned catalyst islands with and without supports by choosing suitable catalyst precursor solutions, and the miniaturized catalytic reaction proceeding on the small catalyst islands will provide a new window for us to observe heterogeneous catalytic reactions.

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