

NOVEL MICROPATTERNED CARBON THIN FILMS BY SELECTIVE CATALYTIC OXIDATION

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Abstract

Patterned carbon thin films find applications in electrodes, lithographic masks, medical devices, biosensors or material coatings designed for lubrication, abrasion resistance, or electrical conductivity. These films can be prepared by carbonization of photoresist polymers using lithographic techniques. However, there is no established method for post-carbonization patterning of carbon thin films due to the lack of suitable liquid etchants as are used for lithographic polymers. This study proposes a new method that uses catalytic oxidation to produce patterned carbon thin films in which molecular oxygen serves as a selective “dry” etchant. Carbon thin films were fabricated by spin coating of a water soluble aromatic followed by carbonization at 700 °C. Solutions of CdCl₂, CoCl₂, CrCl₃, FeCl₃, KCl, MgCl₂, NaCl and NiCl₂ were evaluated as potential catalysts. We use a polydimethylsiloxane stamping technique to transfer catalyst salt solutions onto carbon film in the form of ordered microarrays of droplets and drying pattern of the salt solutions was key to obtaining high-quality micropatterns. The carbon film was then attacked by controlled oxidation at 400 °C to reveal the underlying quartz substrate in the defined circle micropattern. In this study catalyst selection, pattern resolution, feature fidelity and etchant selectivity ratio have been discussed and selective catalytic oxidation has been demonstrated to be a novel method for fabricating patterned carbon thin films.

Introduction

Carbon is a key material for micro-nano devices due to its advantageous properties such as good thermal and mechanical stability. Patterned carbon thin films find application as electrodes, lithographic masks, or material coatings designed for biocompatibility, lubrication, abrasion resistance, or electrical conductivity. Although there are different approaches for patterning organic materials by lithographic techniques (Xia and Whitesides, 1998) such as replica molding (REM), micro-contact printing (μ CP), micromolding in capillaries (MIMIC), there is no established method for post carbonization patterning of carbon thin films. This is primarily due to the lack of suitable liquid etchants as are used for lithographic polymers.

The literature contains one report of carbon film patterning, by locally oxidizing the carbon under the tip of a scanning probe microscope (Muhl et al, 2000). Scanning probe voltage induces local oxidation of the carbon layer directly under the probe tip.

We are interested in exploring the use of molecular oxygen as a selective etchant for carbon. The major factors that affect the rates of carbon combustion are the concentration of active sites on the carbon surface, the surface and pore structure of the carbon, and the presence of catalysts. The intentional addition of metal catalysts has been shown to lead to very high rate enhancements, and the rate acceleration is typically seen only in the immediate vicinity of the catalyst particles. Alkali and alkaline earth metal salts are the oldest known catalysts, which increase the rate of oxidation of carbonaceous materials. After graphite is impregnated with aqueous solutions of soluble metal salts, the catalytic activity for graphite oxidation falls in the order Na > Ba > Sr > Mg > Ca (Amariglio and Duvar, 1966). Similarly, catalytic effects of transition metals and their salts are given as Co > V > Fe > Mn > Cr (Marsh and Taylor, 1977).

In this work we show that molecular oxygen can be used as a dry “etchant” for micropatterning carbon thin films in which the etching selectivity is provided by the use of patterned metal salt catalysts. We use polydimethylsiloxane (PDMS) stamping technique to transfer catalyst salt solutions onto carbon film in the form of ordered microarrays of droplets. Under the correct drying and reaction conditions, we demonstrate here that it is possible to convert these microdroplet arrays into well-defined micropatterned carbon films by controlled catalytic oxidation

Experimental

Carbon thin films used in this study were fabricated by spin coating followed by direct carbonization at 700 °C as in Jian et al. (2005). The spin coating process involved depositing an aqueous solution of an aromatic precursor (indanthrone disulfonate) onto the center of a quartz substrate and then spinning the substrate at around 5000 rpm for 30 seconds leaving a thin film on the surface. After drying, which eliminates solvent and produces a dry organic film, the film was carbonized at 700 °C and then annealed at 1000 °C for further improvement of the film structure. In the present work carbon thin films with 2 μm thickness were prepared by spin coating. The thickness of the film was measured by scanning electron microscopy at high tilt. The structure and combustion properties of these films were also examined by polarized optical microscope and ThermoGravimetric Analysis (TGA) respectively.

Aqueous solutions of catalytic metal were then transferred onto carbon thin films using a PDMS micro-stamping technique. This technique uses an elastomeric PDMS stamp prepared by casting a prepolymer against a silicon master patterned by conventional lithographic techniques. One of the advantages of using elastomer PDMS stamp is its durability. In other words we used the same stamp several times over a long period of time without observing any deformation or loss of function. Figure 1 shows the PDMS stamp we produced having the feature size of 200-micron diameter and the schematic diagram of the stamping technique. Catalytic salt solutions were deposited on a glass slide and then Meyer-bar coating was used to obtain uniform thin film of solution. Desired quantity of the coating is determined by the diameter of the wire used on the rod. After transferring metal salt catalysts solutions to PDMS, the stamps were brought into direct contact with the surface of the substrate, which produced microarrays of droplets on the surface with 200-micron diameter.

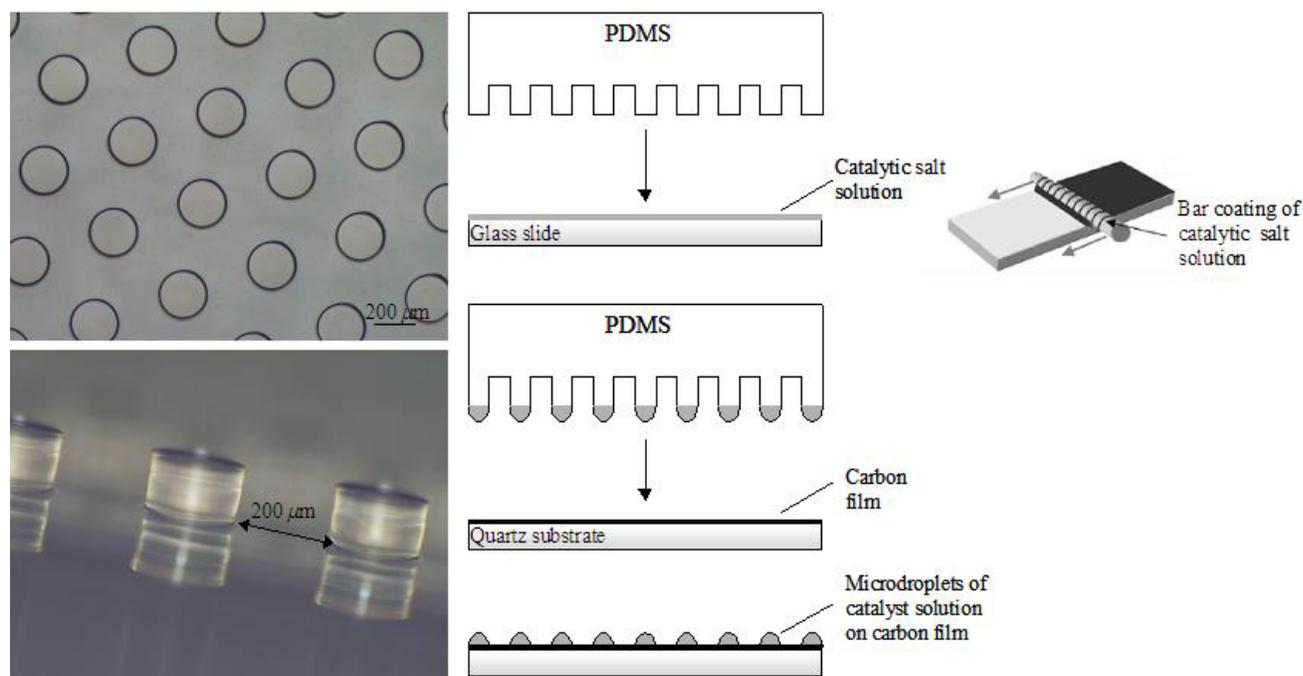


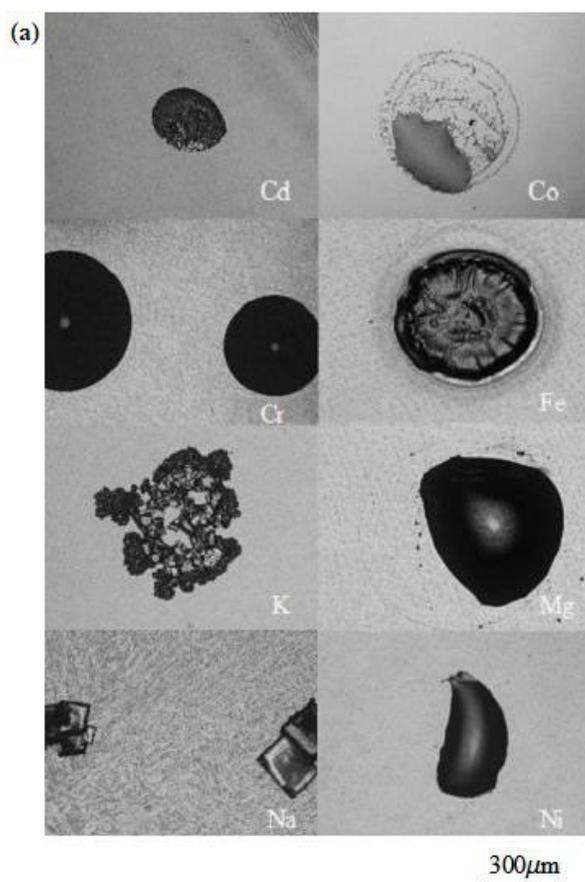
Figure 1: Optical microscope images of PDMS stamp with 200 μm feature size (left), PDMS stamping technique (center), and bar coating technique (right).

After drying at room temperature, the samples were examined under the optical microscope and the dried droplet pattern documented by photography prior to combustion. Then the samples were placed on a ceramic dish and inserted into a quartz tube furnace. After purging with nitrogen gas and reaching the reaction temperature of 400 °C, compressed air was introduced at the flow rate of 300 cc/min for preselected and controlled oxidation times. The reaction was stopped by switching to nitrogen gas. After the furnace cooled the samples were removed, washed with distilled water to remove catalyst, and carefully examined by optical and scanning electron microscopies.

Results and Discussions

Catalyst Screening

Saturated solutions of CdCl₂, CoCl₂, CrCl₃, FeCl₃, KCl, MgCl₂, NaCl and NiCl₂ were evaluated as catalysts in this study. We observed early that the drying pattern of the salt solutions was key to obtaining high-quality micropatterns. Cd, Fe, Mg, K and Ni were observed to give irregular drying patterns that deviated significantly from the desired circular footprint of the original microdroplet. These chloride salt solutions were observed to spread after being transferred onto the carbon film. Instead of spreading, Co chloride showed a coffee drop drying pattern that leads to a dense ring of solids at the outer edge of the original droplet. Figure 2 (a) shows serial images after metal salt catalyst solutions are dried on carbon film. Although, the NaCl drying pattern appears highly nonuniform (a), there is a transparent circular film on the original droplet footprint that is catalytically active (b). We believe the thin film is an adherent adsorbed on the carbon surface and the large crystals are the excess salt above that needed to form the film. In general, both the drying pattern and the subsequent combustion pattern need to be evaluated to choose the best catalyst formulation. Therefore Na and Cr were chosen for further development as micropatterning catalysts.



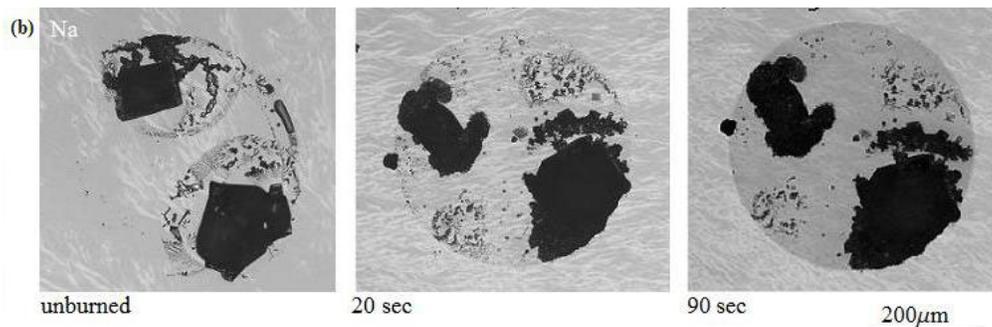


Figure 2. (a) Optical microscope images of NaCl catalyst on carbon following microdroplet deposition and drying. (b) Sodium chloride catalysis occurs through an active but optically invisible salt layer (left), which is revealed only through its selective combustion of the underlying carbon thin film.

After choosing Na and Cr as catalysts to use in this study, the role of solution concentration was investigated by various dilutions of saturated solutions of NaCl and CrCl_3 . Figure 3 shows the result of the dilution of NaCl solution by factors of 1000 (a), 100 (b) and 50 (c). Top row shows the drying pattern of NaCl on carbon film. As the catalyst concentration increases from left to right Na crystals tend to attract each other. After 3 minutes of oxidation (bottom row) it is seen that 50-fold diluted solution of NaCl offers the most desirable catalytic combustion (c). In Fig. 3 (a) it is obvious that the combustion takes place underneath Na crystals only. It can be concluded that when there is not enough catalytic material as in the case of more diluted solutions in (a) and (b), NaCl cannot form a catalytically active transparent film on carbon surface.

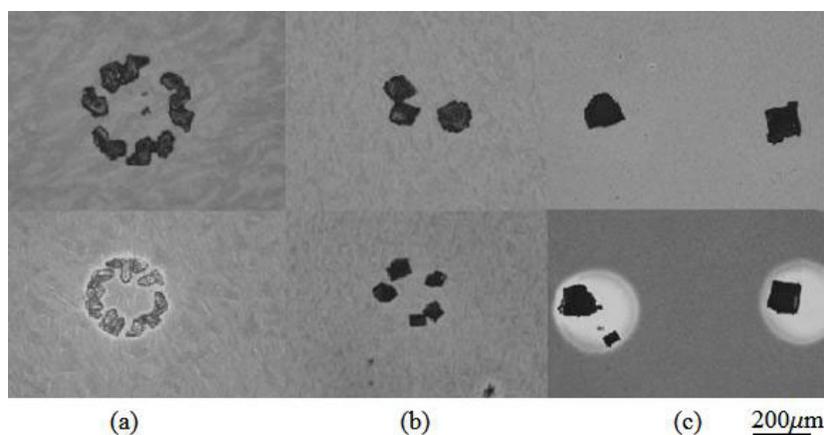


Figure 3. Images of 1000 (a), 100(b) and 50 times (c) diluted NaCl solutions on carbon film before (top row) and after combustion (bottom row).

The selectivity of this etching process can be expressed as the ratio $R_{\text{cat}}/R_{\text{non-cat}}$, which denotes the rate of oxidation with catalysts to that of the unloaded carbon film. The total combustion time of the as-produced (non-catalytic) carbon film at 400 °C is 170 minutes and selectivity ratios are summarized in Table 1.

Table 1: Selectivity ratios of saturated solutions of NaCl, CrCl₃ and CoCl₂ at 400 °C.

Material	R _{cat} /R _{non-cat}
NaCl	80
CrCl ₃	330
CoCl ₂	110

Selectivity ratios were measured as the inverse ratio of the total combustion time in the presence and absence of catalyst. The total catalytic combustion time was determined as the time required at 400 °C in oxygen to completely remove the carbon film in the doped areas and reveal a circle of underlying quartz.

Film Properties

Carbon thin films prepared by spin coating of an aromatic aqueous solution followed by carbonization at 700 °C show liquid crystalline structure under polarized light (Jian et al., 2005). The surface is uniform, dense and entirely anisotropic. Figure 4 compares the reaction rates of as-produced (non-catalytic) and NaCl loaded carbon films. The as-produced carbon film starts burning at 550 °C whereas the reaction initiates below 550 °C with the NaCl doped carbon film as expected. In both cases the reaction is complete by about 900 °C. A temperature of 400 °C was selected for the micropatterning process since the TGA data in Fig. 4 indicates that the noncatalytic rate is very slow, but the temperature is just above the reaction initiation point where the catalytic rate proceeds quickly.

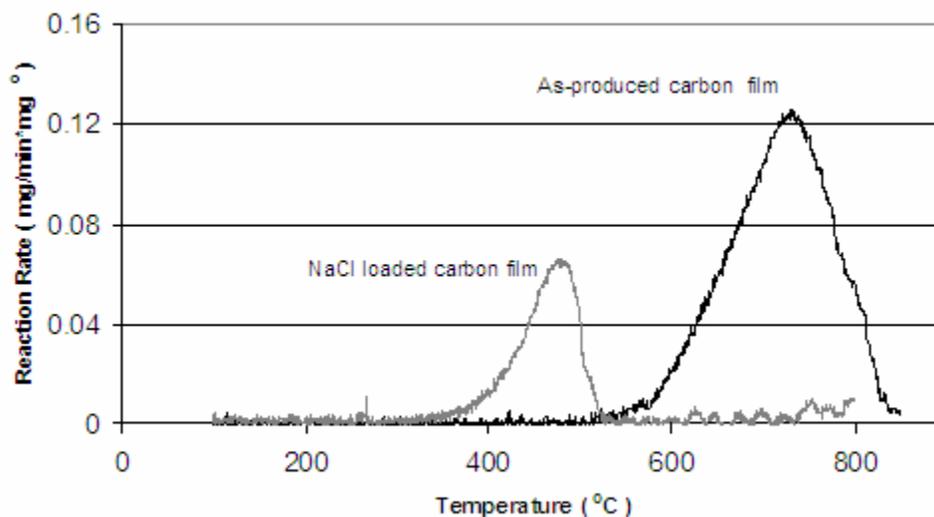


Figure 4: Reactivity plots of the raw and NaCl loaded carbon films in air in TGA. In the Y-axis label, mg⁰ refers to the initial unreacted weight of the sample.

Micropatterning

Sodium and chromium salts were transferred to the carbon film from the PDMS stamp followed by drying and oxidation for 3 minutes at 400 °C resulted in a well-defined micropatterned carbon film as shown in Figs. 5 and 6, respectively. It is seen that sodium salt is transferred onto the carbon film with an ordered manner although circle pattern is not visible with the optical microscope. After oxidation of 3 minutes, the SEM image shows that 200 μm diameter circle pattern is obtained successfully on carbon film by PDMS stamping technique.

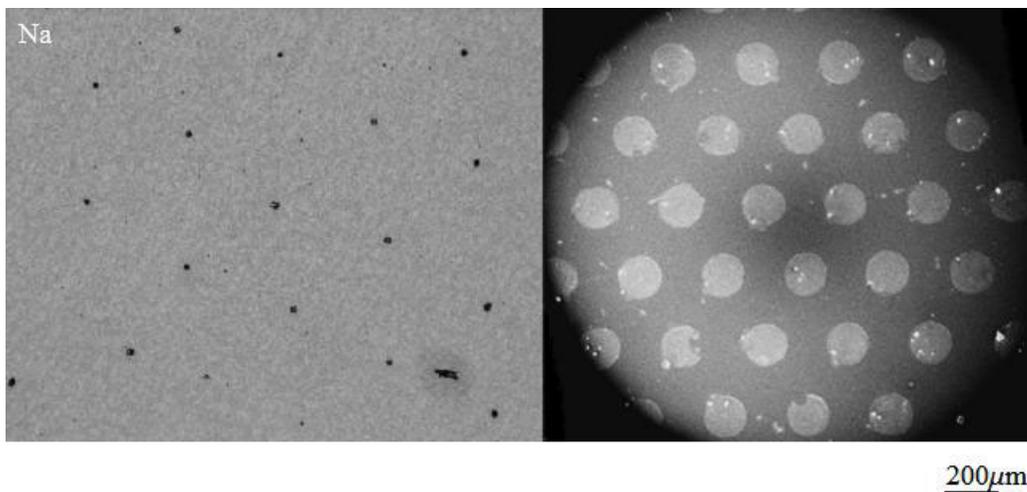


Figure 5. Optical microscope image of carbon film after loading with Na (left), and SEM image of carbon film after 3 minutes oxidation without washing (right)

Similarly, the chromium salt is well transferred onto the carbon film, which is then attacked by controlled oxidation to reveal the underlying quartz in the defined circle micropattern. After catalytic oxidation, liquid crystalline structure of the carbon film is not observed in the areas of circle micropattern (Fig. 6) proving that the selective catalytic combustion produces well defined patterned carbon thin films in which oxygen is the dry etchant.

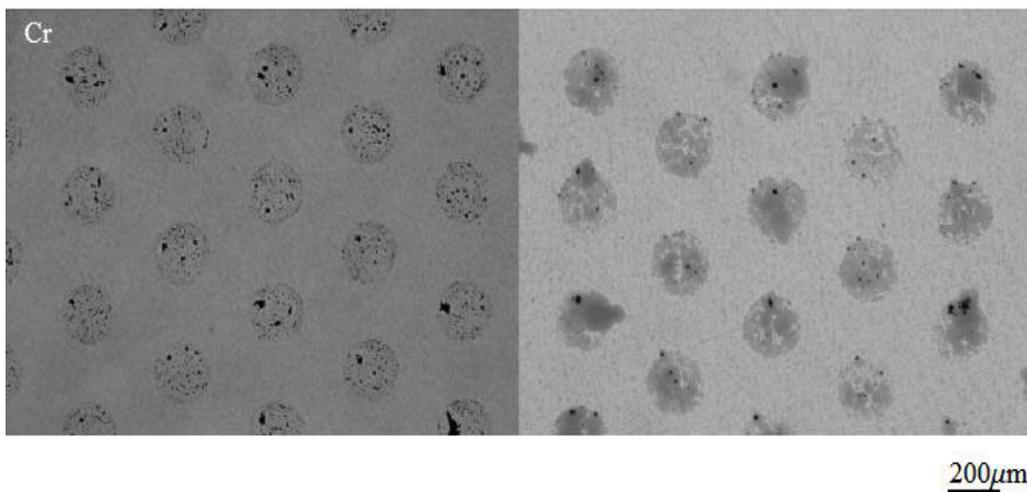


Figure 6. Microscope images of patterned carbon film after loaded with Cr (left) and after 3 minutes oxidation without washing. (right).

Conclusions

In this paper we demonstrated the new micropatterning technique for carbon thin films in which molecular oxygen is used in combination with micropatterned metal salt catalysts for selectively etching carbon. We studied the overall suitability, which includes drying patterns, rate enhancement, and other factors such as the formation of dense deposits that block the rate. Our results indicate that the selection of metal salt catalysts markedly affects the patterning resolution and the etchant selectivity ratio. Among all metal salts that are screened, CrCl₃ and NaCl appear to be most suitable and further work is underway to refine the process. In other words, Cr and Na chlorides show the most promise for catalytic combustion micropatterning. In conclusion, selective catalytic oxidation of the carbon thin film using metal salt catalysts appears to be a highly promising method for micropatterning of carbon thin films.

Acknowledgments

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