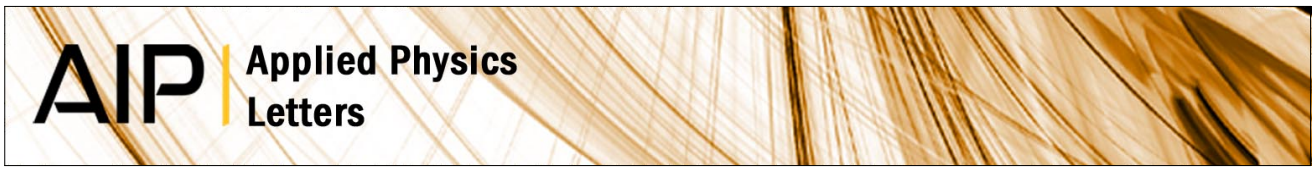

Ultraviolet laserprojection patterning of polymeric materials for electrochemical gas sensors

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Ultraviolet laser-projection patterning of polymeric materials for electrochemical gas sensors

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ArF laser ablation has been successfully applied to maskless pattern by projection lithography of two polymeric materials, polysiloxane and polyHEMA (2-hydroxy-ethyl methacrylate), to be used as gas diffusion membranes in electrochemical gas sensors. Etch rates up to 0.65 μm/s with smooth surface morphology, high edge definition, and a resolution of $\sim$5 μm were obtained using laser fluences between 250 and 400 mJ/cm^2 and repetition rates between 1 and 10 Hz in air for polyHEMA films and in nitrogen for polysiloxane films.

Electrochemical gas detectors based on amperometric measurements made with electrodes covered by polymer membranes have been fabricated and investigated in depth since the introduction of the Clark cell in 1956.[1–6] Although such detectors have several intrinsic advantages over catalytic and semiconductor gas sensors, such as low operating temperature, lower power consumption, and the possibility of achieving gas selectivity, they have seldom been miniaturized and realized with integrated circuit (IC) compatible methods. Of particular interest is a recently reported type of sensor, the triple-point sensor,[2] in which a three-dimensional solid-state structure is covered by a gas diffusion polymeric membrane that has to be chemically functionalized to achieve three functions. It should give selectivity for the gases of interest, guarantee a good adhesion to the solid-state structure, and finally, it should have the possibility of photopolymerization. Battiliotti *et al.*[5] have recently described the preparation of a new sensitive membrane by a technique compatible with IC technology. The method described by these authors consists in the introduction of amino groups onto the surface of the solid-state device by reacting the surface silanol groups present in SiO_2 or Si_3N_4 with suitable functionalized organosilanes such as 3-(2-aminoethyl) aminopropylsiloxane, followed by the coupling of the hydroxyl moiety of 2-hydroxy-ethyl methacrylate (HEMA) with the said amino function, carried out by means of different difunctional condensing agents.

The aim of this work is to evaluate the possible utilization of the excimer laser ablation technique to pattern by projection lithography polysiloxane and polyHEMA films to be used as gas diffusion membranes in electrochemical gas sensors. In the following, the effect of the main process parameters, such as laser fluence, laser repetition rate, and gas ambient on etch rate, surface morphology, resolution, and selectivity with respect to the SiO_2/Si bottom layer are examined and discussed.

The experimental setup consisted of an ArF excimer laser, an optical system, and an X-Y positioning stage on which the samples were mounted perpendicularly to the laser beam. The ArF Laser (Lambda Physik LPX 200i) could emit 300-mJ pulses of 17-ns duration at 193 nm and repetition rates up to 50 Hz. The central part of the beam cross section was apertured by a 5×5 mm^2 slit, condensed by a 200-mm focal length lens, and imaged through a Cr on quartz mask by means of a 15× Schwarzschild microscope objective (NA =0.28), to give an irradiated area on the sample of $\sim$170 ×440 μm. The mask pattern consisted of an array of 1-mm-diam holes in a matrix of 0.14-mm-wide perpendicular lines. The laser fluence on the samples was varied between 250 and 500 mJ/cm^2 and the repetition rate was kept at $\leq$10 Hz. Ablation experiments were performed at room temperature in air or under N_2 flow to avoid redeposition of debris. The samples were 50–200 μm thick polyHEMA films deposited on SiO_2/Si wafers by spin coating. Etch rates were determined by dividing the ablated depth measured with a Taylor–Hobson mechanical stylus by the number of laser pulses emitted during the experiment. The laser fluence was measured using a pyroelectric joulemeter. Etched surface morphology and cross sections were examined in a Hitachi S-800 field emission scanning electron microscope.

PolyHEMA films were cleanly etched by 30–35 mJ laser pulses at 193 nm, with laser fluences ranging from 250 to 300 mJ/cm^2. Increasing the laser fluence on the samples resulted in higher etch rates, but above $\sim$303 mJ/cm^2 ablation of the bottom SiO_2 layer impeded the obtention of selective etching with respect to this material. The influence of the pulse repetition rate on the ablation process is shown in

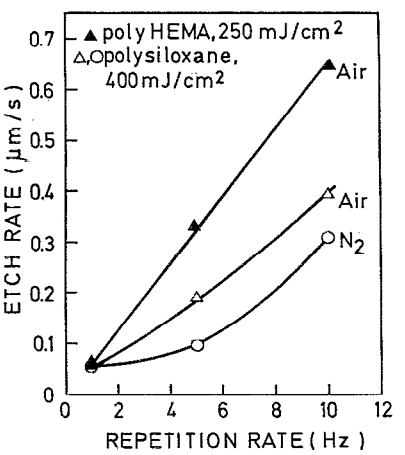

FIG. 1. Etch rate dependence on laser repetition rate for polyHEMA films in air (▲), polysiloxane films in air (△), and nitrogen (○), respectively.

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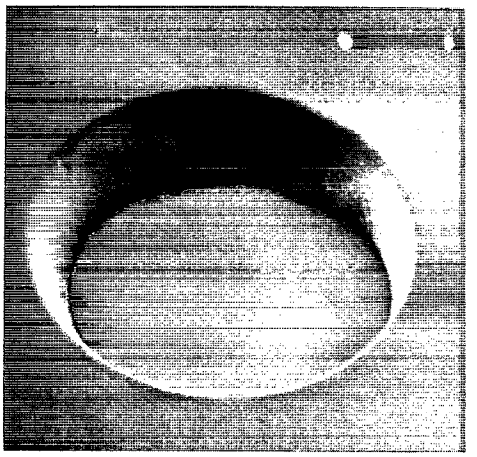

FIG. 2. Etch morphology of a polyHEMA film patterned in air at a laser fluence of 250 mJ/cm^2 and a repetition rate of 5 Hz. (Magnification scale: 15 μm.)

Fig. 1. The etch rate per second for polyHEMA films irradiated at 250 mJ/cm^2 in air is plotted against the pulse repetition rate. It can be seen in this figure that the etch rate increases with the repetition rate, the former being more than ten times greater at 10 Hz than at 1 Hz. In consequence, it is worth working at 10 Hz, as no sign of thermal damage of the film surface has been observed at this repetition rate. The scanning electron micrograph shown in Fig. 2 illustrates the etch morphology of a 20-μm-thick polyHEMA film patterned in air at a laser fluence of 250 mJ/cm^2 and a repetition rate of 5 Hz. The surface morphology around the ~50-μm-diam etched hole depicted in the figure is very smooth and shows no evidence of thermal damage in the form of cracking or melting of the polymeric material. Moreover, the ablation process does not generate redeposition of material on the surface or the etched features, allowing the obtention of clean and smooth walls and bottom morphologies. The scanning electron microscopy (SEM) photograph of Fig. 3 shows a cross-sectional view of the minimum feature size (~5 μm) obtained in polyHEMA films with the projection setup used in our experiments. It should be noted in this micrograph the good edge definition obtained in this material by the laser ablation technique.

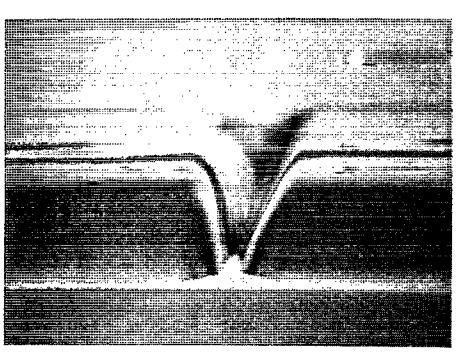

FIG. 3. SEM cross-sectional view of the minimum feature size obtained in a ~20-μm-thick polyHEMA film by laser projection lithography. (Magnification scale: 20 μm.)

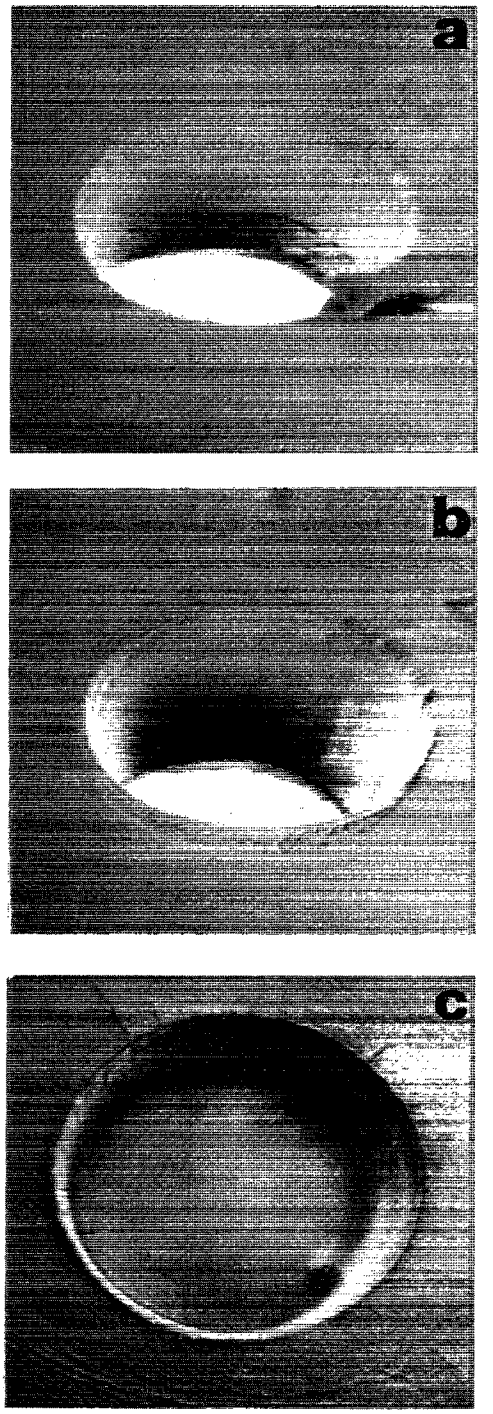

FIG. 4. Effect of laser fluence and gas ambient on polysiloxane etch morphology: (a) 400 mJ/cm^2 and 10 Hz in air; (b) 400 mJ/cm^2 and 10 Hz in nitrogen; and (c) 500 mJ/cm^2 and 10 Hz in nitrogen. (Magnification scale: 20 μm.)

In contrast with polyHEMA films, that have a strong absorption at the ArF laser wavelength (193 nm) attributable to the ester groups,[7] polysiloxane films exhibit lower photosensitivity due to the high silicon content in the polymer backbone,[8] which results in lower absorption at the same wavelength. In consequence, a laser fluence of at least ~330 mJ/cm^2 is required to induce photoablation of this polymer. At a laser fluence of 400 mJ/cm^2, for instance, the observed

etch rates of polysiloxane films in air are considerably lower than those for polyHEMA samples at 250 mJ/cm^2, although the etch rate dependence on the repetition rate follows a similar trend, as depicted in Fig. 1. The utilization of a nitrogen flow over the polysiloxane samples during the ablation experiments tends to decrease the etch rate, but it helps removing the ablated material that redeposits in the etched hole and on the nonirradiated surface. When the laser fluence is increased above 500 mJ/cm^2, we have observed a morphological transition from smoothly to roughly etched surfaces accompanied by signs of thermal damage. The SEM photographs shown in Fig. 4 illustrate the effect of laser fluence and gas ambient on polysiloxane etch morphology. Figures 4(a) and 4(b) correspond to a polysiloxane film patterned at a laser fluence of 400 mJ/cm^2 and a repetition rate of 10 Hz in air and nitrogen, respectively. It is evident from these micrographs that the surface morphology using this laser fluence is very smooth and shows no indication of thermal damage. The edge definition of the ~65-μm-diam etched holes is not as good as the one observed in polyHEMA films, but this could be a consequence of a nonperfectly focused laser beam. On the other hand, the utilization of a nitrogen flow over the polysiloxane sample during the laser ablation experiments is necessary in order to avoid the redeposition of ablated material and obtain clean and smooth etched walls and bottom morphologies. The SEM micrograph showed in Fig. 4(c) corresponds to the same polysiloxane film patterned in nitrogen using a laser fluence of 500 mJ/cm^2 and a repetition rate of 10 Hz. As it was mentioned above, at this high laser fluence, the polymeric film surface evidences signs of thermal damage such as cracks and rough morphology as well as melting around the edge of the etched hole. Therefore, it is of critical importance to operate at laser fluences just sufficient or slightly above the threshold to start photoablation of the polymer in order to obtain acceptable etch morphologies using the laser ablation technique.

Finally, given that the laser fluence threshold for photoablation of polysiloxane is approximately 30 mJ/cm^2 greater than that for SiO_2; it was not possible to obtain selective etching of the polymeric film with respect to the SiO_2 bottom layer. This is a technological issue that needs to be addressed in order to apply the laser ablation technique to the patterning of polysiloxane films to gas sensors fabrication. The use of an *in situ* optical technique that will allow for the accurate determination of the polymer etch end point will probably be most useful in solving this problem.

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