

THIN FILM PATTERNING USING A WATER-SOLUBLE ETCH MASK

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ABSTRACT

We present a novel method to pattern materials which are not compatible with organic solvents through the use of a water-soluble etch mask. In this work we used a polyvinyl alcohol (PVA) etch mask to pattern polystyrene-based optical oxygen sensor films. We demonstrate a manual PVA deposition method utilizing a micromanipulator stage and syringe; however, the PVA could also be deposited using a 3D or multilayer inkjet printer. Following PVA deposition, the polystyrene sensor film is patterned using an oxygen plasma etch. Sensor function after patterning was verified by oxygen gas calibration. The simplicity of this fabrication process makes it well-suited for applications in microfluidic cell culture and labs on a chip, as many of these applications require single-use sensors.

KEYWORDS: Thin-film Patterning, Optical Oxygen Sensor, Microfluidics, BioMEMS, Lab-on-a-chip

INTRODUCTION

The micropatterning of certain solvent-incompatible thin films presents a difficult problem because photoresist solvents, developers, or strippers attack the film. While it is possible to directly deposit some of these materials using methods such as pipetting, inkjet printing, or microcontact printing, these methods often yield patterned films of nonuniform thickness. An example application where film thickness uniformity is an important parameter is optical oxygen sensing using intensity-based fluorescence or phosphorescence quenching measurements. In this application, the luminescence intensity is used to directly measure the oxygen levels; however, this intensity is also dependent on the amount of luminescent indicator present, and hence the film thickness. Spin casting the sensor film onto flat substrates and subsequent patterning yields more uniform sensor film thickness than direct deposition (e.g. through pipetting) of sensor areas, which facilitates intensity-based oxygen measurements as the sensor's light emission is dependent on film thickness. This paper presents a simple and cost-effective method of patterning these spin-cast films using a water-soluble polyvinyl alcohol (PVA) etch mask.

BACKGROUND

Optical oxygen sensors are ideal for microfluidics and lab on a chip systems because they do not consume oxygen and can be readily miniaturized. The luminescence quenching behavior of the sensors is modeled by the Stern-Volmer equation [1], where I_0 and I are the emission intensities at zero oxygen and oxygen partial pressure pO_2 , respectively, and K_{SV} is the Stern-Volmer quenching constant:

$$\frac{I_0}{I} - 1 = K_{SV} pO_2 \quad (1)$$

Our sensors use phosphorescent platinum octaethylporphyrin ketone (PtOEPK) [2] as the oxygen-sensitive indicator molecule, encapsulated in thin spin-cast polystyrene films. Because common photoresist solvents, developers, and removers attack the polystyrene matrix of the sensor, traditional photolithography or e-beam lithography cannot be used to pattern these types of sensor films without the use of a pinhole-free metal etch mask [3, 4], which necessitates a multi-step process. Other methods previously presented for fabricating these types of sensors include the use of polydimethylsiloxane (PDMS) etch stamps [5] and hot embossing into an ethylene-vinyl-alcohol (EVOH)/PDMS double-layer [6]. Although the PDMS stamp method is a single-step process employing a reusable stamp, fidelity of pattern transfer was highly dependent on the type of plasma etcher and etch parameters used.

We present a simple, alternative fabrication method that can be used to pattern such solvent-incompatible materials. PVA has been previously demonstrated as a masking layer used while patterning biomolecules using photolithography to prevent the photoresist from coming into direct contact with the biomolecules [7]. Similarly, a lift-off process using a PVA/SU-8 bilayer has been demonstrated for the fabrication of organic thin-film transistors [8], and PVA has also been demonstrated as an SU-8 structure release layer for MEMS applications [9]. While these methods are capable of very high resolution features, they require photolithographic processing of each substrate. Because many of the applications of microfluidic and lab-on-a-chip devices necessitate inexpensive single-use devices, minimal processing to fabricate each sample is an advantage. Our method is faster, easier, and less expensive than the photolithographic methods, and presents a promising alternative for applications where the resolution is less important than the speed and cost.

EXPERIMENTAL

Figure 1 presents the fabrication process flow for the process applied to the fabrication of optical oxygen sensors. We chose PVA for the etch mask material because it is water-soluble (and thus can be dissolved without damaging the sensor) and can be patterned in sufficiently thick films to serve as an etch mask. We demonstrate a manual dispensing method, using a syringe and micromanipulator stage; however, the PVA could also be deposited using a 3D or multilayer inkjet printer.

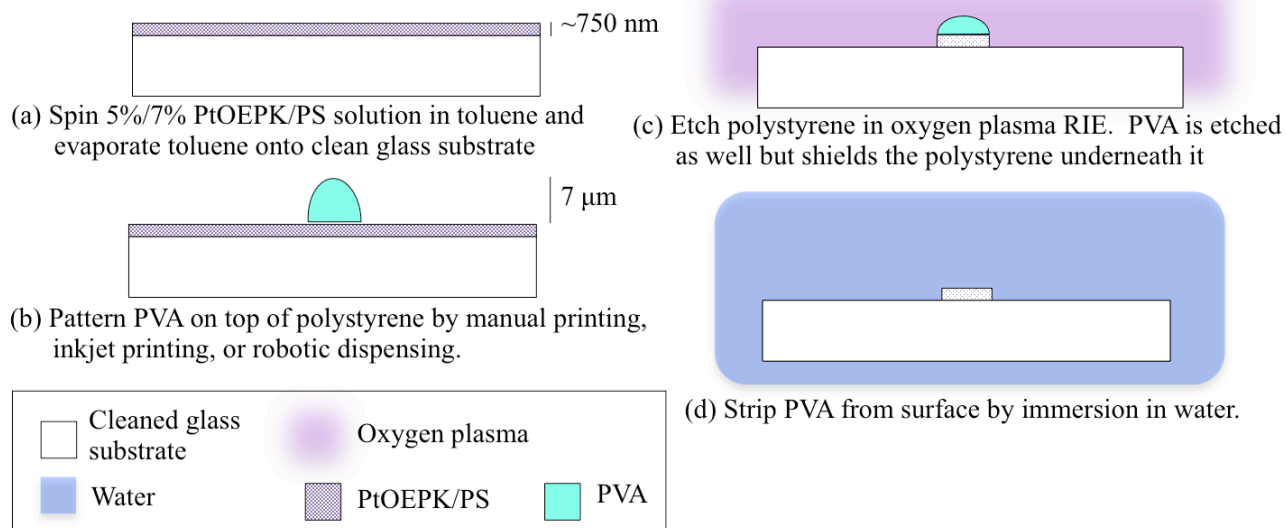


Figure 1. Oxygen sensor fabrication process using a PVA etch mask. (a) Sensor film spin. (b) Patterning of 10% (w/w) solution of PVA in water. (c) Exposure to oxygen plasma (Technics Planar Etcher II, $P=400$ mTorr and $P=160$ W, $t=12$ minutes). We measure average etch rates of 90 nm/min for the PVA and 86 nm/min for the polystyrene. (d) PVA strip.

Etch completion was verified with profilometry using a Dektak 150 profilometer and fluorescence microscopy using a Nikon TE2000U fluorescence microscope system. A filter set for measuring the phosphorescence of the PtOEPK dye (Omega Optical 400AF30 bandpass excitation filter, 475DCLP longpass dichroic mirror, and 700ALP longpass emission filter) was used for the fluorescence microscopy characterization. Oxygen sensor function after patterning using PVA etch masks was verified by calibration using three gaseous oxygen concentrations (0 atm, 0.21 atm, and 1 atm). Briefly, the sensors were exposed to pure gaseous nitrogen, air, and oxygen and the sensors' phosphorescence intensities were measured at each of these known oxygen concentrations. The quenching characteristics of four separate oxygen patches were determined and averaged, with each patch being calculated on an average of 25 000 pixels.

RESULTS AND DISCUSSION

Figure 2 and Figure 3 present the phosphorescence sensor images and the profilometry results of the patterned sensors, respectively. The thickness uniformity of the PVA film does not have an effect on the patterning results, as long as the film had a minimum thickness large enough to withstand the oxygen plasma etching time required to etch the oxygen sensor film. For our sensor film thickness of approximately 750 nm, we found that 5 μm of PVA was sufficient.

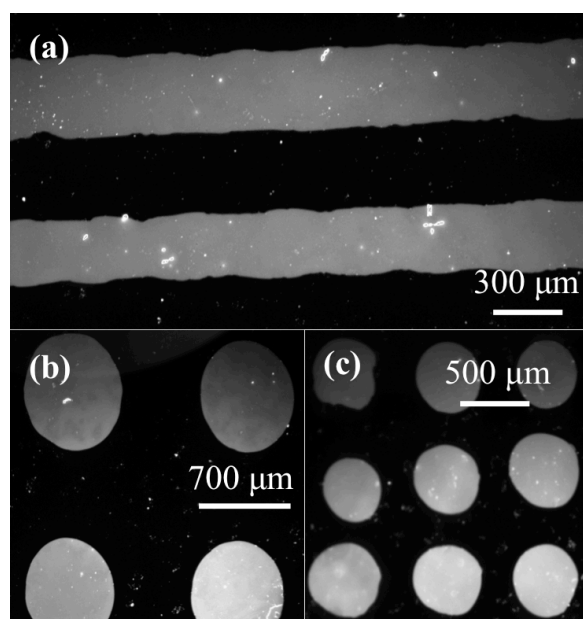


Figure 2. Phosphorescence images of patterned oxygen sensor (a) lines, (b) larger patches, and (c) smaller patches, acquired using a fluorescence microscope.

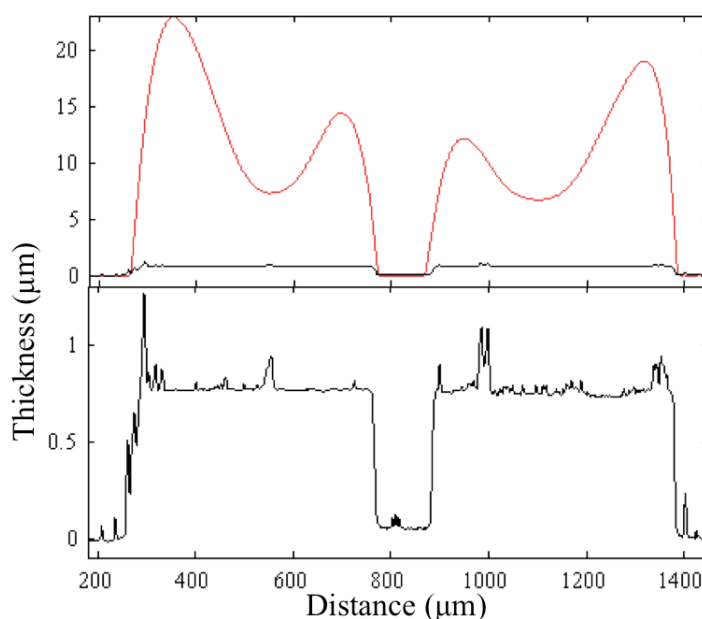


Figure 3. Profilometry measurement of (top) PVA film before etching (red) and patterned sensor film after PVA strip (black), and (bottom) close-up of patterned sensor film after PVA strip, acquired using a Dektak 150 profilometer.

The sensor calibration conducted after patterning verified that the oxygen sensors remained functional. The sensor performance (shown in Figure 4) was found to demonstrate a linear Stern-Volmer quenching relationship, as was expected from Equation 1 and observed in the sensor films before the patterning process.

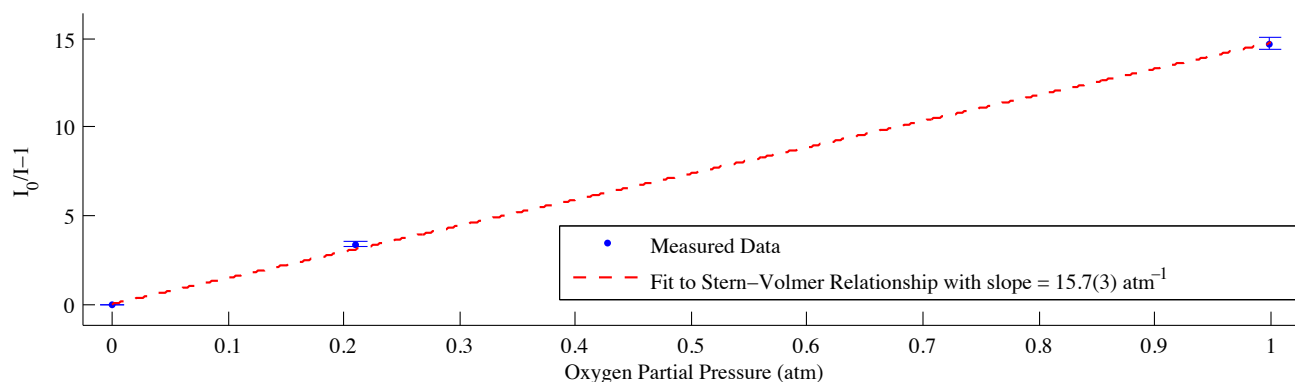


Figure 4. Measured phosphorescence quenching behavior of patterned optical oxygen sensors (blue datapoints), fit to the Stern-Volmer relationship shown in Equation 1 (red dotted line). The patterned sensors exhibited linear quenching behavior with an unquenched intensity (I_0) of 157 and a quenching constant (K_{SV}) of $15.7(3) \text{ atm}^{-1}$.

CONCLUSION

We have demonstrated a simple method for micropatterning solvent-incompatible thin films using direct-deposition of a water-soluble PVA etch mask, and we have validated this process by micropatterning a polymer optical oxygen sensor film. The process could also be a convenient method for patterning other polymers or even biomolecules, for applications in lab-on-a-chip and other systems.

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