

APPLICATION OF RAPID EXPANSION OF SUPERCRITICAL SOLUTIONS FOR THE DEVELOPMENT OF MICROFABRICATED SENSORS

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Rapid Expansion of Supercritical Solutions (RESS) was used to develop polymer nanoscale materials for sensing applications. The advantages and limitations of using supercritical fluid solvents for the production of polymer-based sensors are discussed. It is demonstrated that, by carefully selecting and controlling the RESS processing conditions, it is possible to produce various nano and micro scale polymer coatings suitable for microfabricated chemical sensors with enhanced sensitivity and selectivity.

INTRODUCTION

Nanoscale polymeric materials have the potential to dramatically improve the performance of a variety of sensor systems. Examples include microfabricated chemical and biological sensors incorporating polymer films and particles, polymer-coated microchannels and molecularly imprinted materials as well as radiation detectors and physical sensors based on polymer nanocomposites. However, polymers typically have a very low vapor pressure and are, therefore, not compatible with the conventional vapor-phase processing strategies employed by the microelectronics industry to produce materials and devices at submicron dimensions. The integration of nanoscale polymeric materials into sensor systems has proven difficult to achieve using liquid solvents because of viscous effects and the need to separate the polymer from the solvent. It is well-known that Rapid Expansion of Supercritical Solutions (RESS) can be used to produce a variety of micro and nanoscale morphologies as well as mixtures of materials [1-2]. RESS has the additional advantage of being a spray-on technique that can deliver dry micro and nanoscale precipitates onto a substrate from the expanding gas-phase.

1. POLYMERS FOR MINIATURE SENSORS AND COATING TECHNIQUES

The miniaturization of chemical sensor technology normally requires the controlled interfacing of a chemically sensitive/responsive coating material with an appropriate microfabricated transduction device. A variety of miniature transducers are available and include; acoustic (e.g. SAW, BAW), optical (e.g. SPR, optical probes) and impedemetric devices as well as capacitance based structures such as MEMS cantilevers. Each type of transducer, when interfaced to an appropriate chemically sensitive material, has the potential to convert chemical interactions into a measurable output signal. However, for optimal performance, the coating requirements for these microscale devices are stringent and the coating thickness and uniformity must be precisely controlled at the nanoscale. For example, the optimal coating thickness for surface acoustic wave devices of 200-500 MHz resonance frequency must be on the order of 20-100 nm, depending on the polymer properties [3]. Usually rubbery polymers such as poly(isobutylene) (PIB), poly(dimethylsiloxane) (PDMS),

75% methylphenyl-25% diphenylsiloxane (OV-25), fluoropolyol (FPOL), poly(epichlorhydrin) (PECH) are used for chemical sensing applications [3,4].

The air-brush method is commonly employed for the deposition of polymeric materials onto microfabricated transducers [4] and is schematically depicted in Figure 1b. Figure 1a is a schematic diagram of the RESS process for comparison. The air-brush spray-on method utilizes conventional liquid solvents containing a dissolved polymer and dispersed by a propellant gas. The average droplet size produced by an air-brush typically ranges from 20-50 micrometers, which is at least an order of magnitude larger than desired for coating a microscale device. Additionally random macroscopic defects are formed throughout the coating as a result of solvent evaporation and polymer shrinkage.

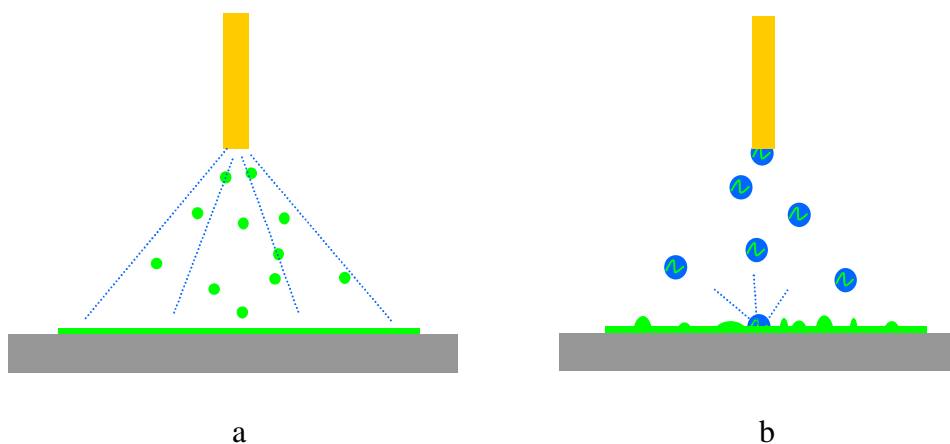


Figure 1. Schematic of RESS (a) and air brush (b) spray-on techniques

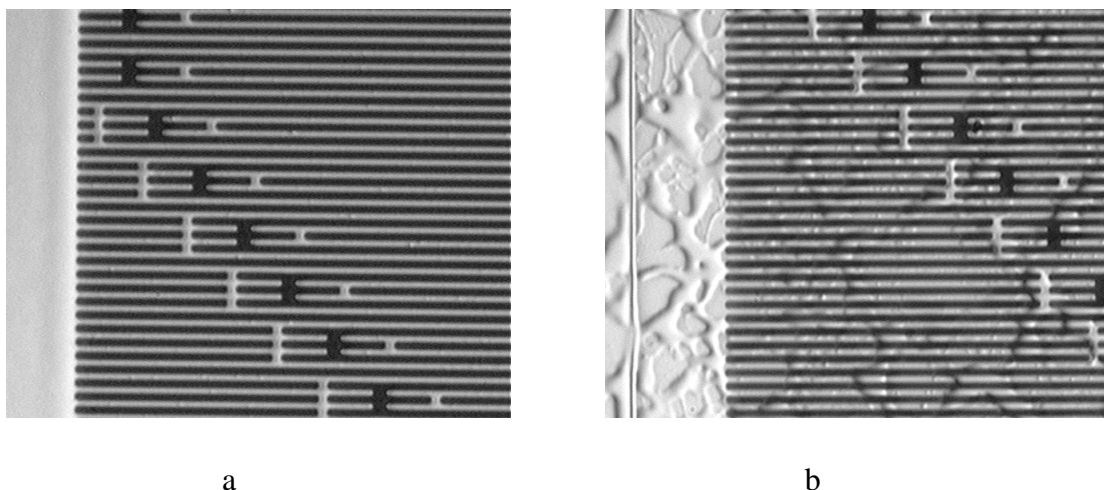


Figure 2. PIB coating deposited by RESS (a) and by airbrush (b) on SAW device

On the other hand, it has been well established, both theoretically and experimentally, that RESS precipitates can be formed well into the nanoscale. Based on previous investigations and our own experiments we have developed a qualitative approach for selecting the RESS

processing conditions, which will result in nanoscale precipitates [5]. To preserve the particle morphology and achieve good coating uniformity, the solute particles must be solvent-free before reaching the substrate. Thus, the RESS expansion path should not cross the liquid-vapor equilibrium curve of the solvent and the nozzle-to-substrate distance must be optimized. In order to achieve adequate thickness control and reproducibility, the process must be automated to control the deposition time to within fractions of a second [5]. Figure 2 shows the surface of a SAW device coated with an equivalent thickness of PIB polymer deposited by RESS (a) and by air brush (b). The distance between interdigital electrodes is 3 micrometers. As can be seen in the figure, the air-brushed coating contains a random pattern of microscale defects, while the RESS coating consists of a highly uniform defect-free film. We have previously demonstrated that most of the common sensing polymers, including PIB, OV-25, siloxane-based polymers, and others can be dissolved in supercritical solvents, such as pentane, butane, chlorodifluoromethane, and even CO₂.

2. GLASSY AND CRYSTALLINE POLYMER COATINGS AS NEW SENSOR MATERIALS

Glassy polymers, even though they exhibit favorable chemical properties, have not generally been utilized as sensor coatings. The major draw back was their mechanical properties, such as high modulus and low elongation, which can result in coating delamination and cracking. For example, SAW devices were found to exhibit significant signal degradation when loaded with a glassy polymer. In our previous work we demonstrated that RESS is a suitable technique for the deposition of glassy polymers onto microscale sensors in the form of nanoscale particles. We demonstrated that coatings consisting of glassy polymer particles do not interfere with the acoustic wave propagation as long as the particle diameter is small compared to the acoustic wavelength [5,6]. In fact, particulate coatings, because of the very high surface to volume ratio, resulted in a significant improvement in sensor sensitivity. Figure 3 below illustrates that effect for a particular fluorinated glassy polymer.

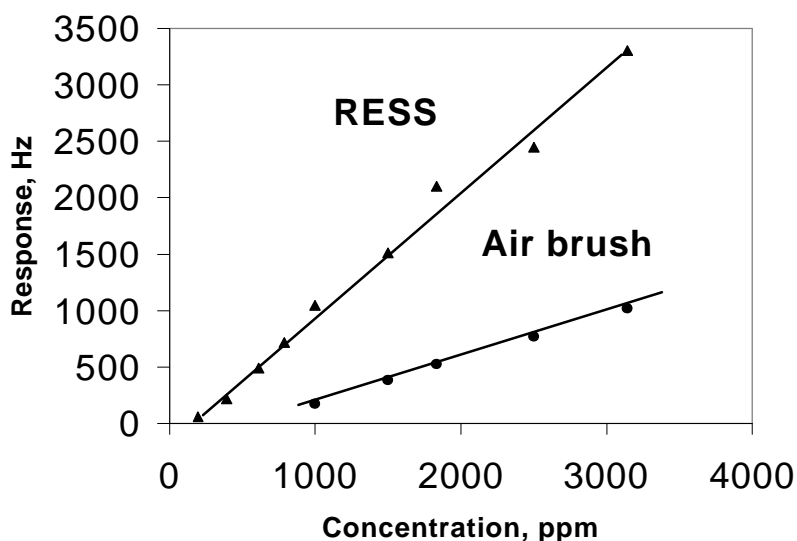


Figure 3. FAA coated SAW sensor response to methanol vapor

An equivalent mass of fluoroalkyl acrylate (FAA) glassy polymer was deposited onto the surface of 250 MHz SAW transducers (resonance device) using both the air-brush and RESS deposition methods. The average coating thickness was equal to about 30 nm as calculated based on the 200 kHz frequency shift of the SAW devices. The RESS coating consisted of about 100 nm diameter particles and exhibited a sensitivity enhancement of about 450% to toluene vapor in comparison to the air-brush deposited film. The polymer-vapor interaction for this system is dominated by surface adsorption. Therefore, the vapor sensitivity is expected to be a strong function of the polymer surface area.

In addition to SAW transducers we have found that by RESS it is possible to deposit rubbery or glassy polymers onto a variety of microscale devices such as MEMS cantilevers and microchannels. It is difficult to deposit polymers onto microscale assemblies using traditional wet spray-on techniques, because the size of the liquid droplet is on the same scale or even larger than the devices themselves. Figure 4 is a before and after image of a microscale cantilever coated with crystalline polymer nanoparticles using RESS, illustrating that RESS can be successfully used to coat micro structured devices.

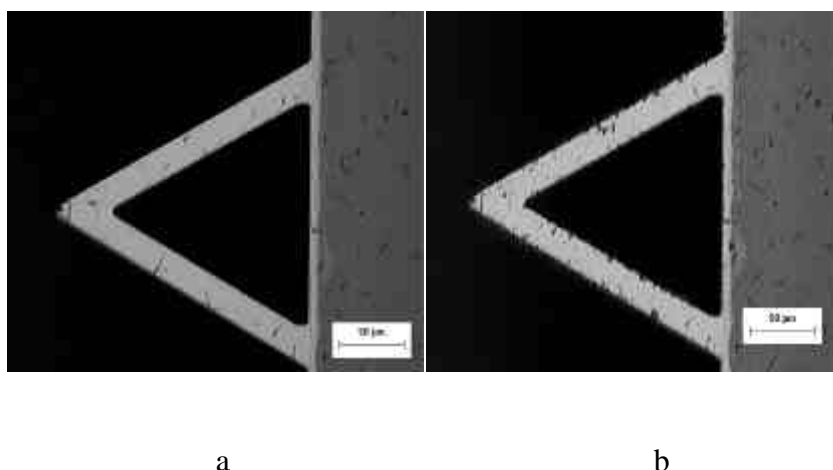


Figure 4. AFM cantilever before (a) and after RESS coating (b) by crystalline polymer.

3. ADVANCED POLYMER COATINGS FOR SENSOR APPLICATION

RESS has been previously utilized to precipitate composite particles from supercritical solutions containing more than one dissolved solute [2]. It has also been used for the development of novel materials in nonequilibrium states by taking advantage of the extremely rapid kinetics of the phase separation [7,8,9]. We have employed RESS to produce nonequilibrium amorphous particles that can be recrystallized through exposure to a plasticizing vapor directly on the sensor surface. Figure 5 is an SEM image of a highly crystalline diolefinic compound (2,5-distyrylpyrazine (DSP)) developed by RESS in an amorphous state (a) and recrystallized by vapor (b) [8-9]. We have found that the resulting crystalline particles retain a molecular scale porosity that is characteristic of the plasticizing vapor and can, therefore, be used to develop microscale sensors with enhanced selectivity to specific molecular species [9].

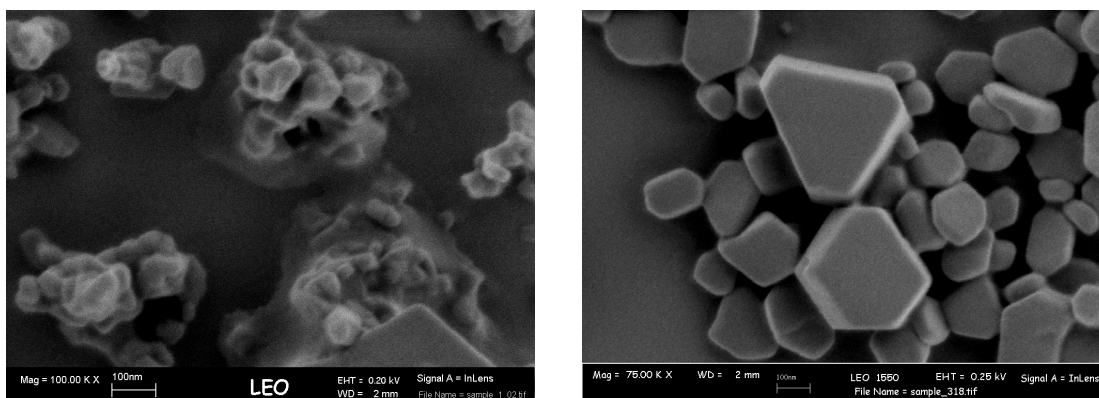


Figure 5. Highly crystalline diolefinic compound 2,5-distyrylpyrazine (DSP) developed by RESS (a) and recrystallized by vapor (b). Scale bar is 100 nm.

We have also used RESS to develop chemically modified particles and polymer nanocomposites directly on the sensor surface. RESS precipitates of a single solute were deposited in a surface and modified through exposure to either a chemical vapor or a source of energy such as UV light or temperature in order to induce cross-linking and/or polymerization. The resultant coating exhibited superior properties, such as improved adhesion and mechanical integrity that influences the signal quality and sensor long-term stability. Additionally, the modification can even improve overall sensor sensitivity and selectivity. For example, figure 6a is an SEM image of bis(12 hydroxystearate) terminated poly(dimethylsiloxane) (PDMSH) particles developed by RESS and crosslinked by 2,4-toluenediisocyanate (TDI) vapors at room temperature [10].

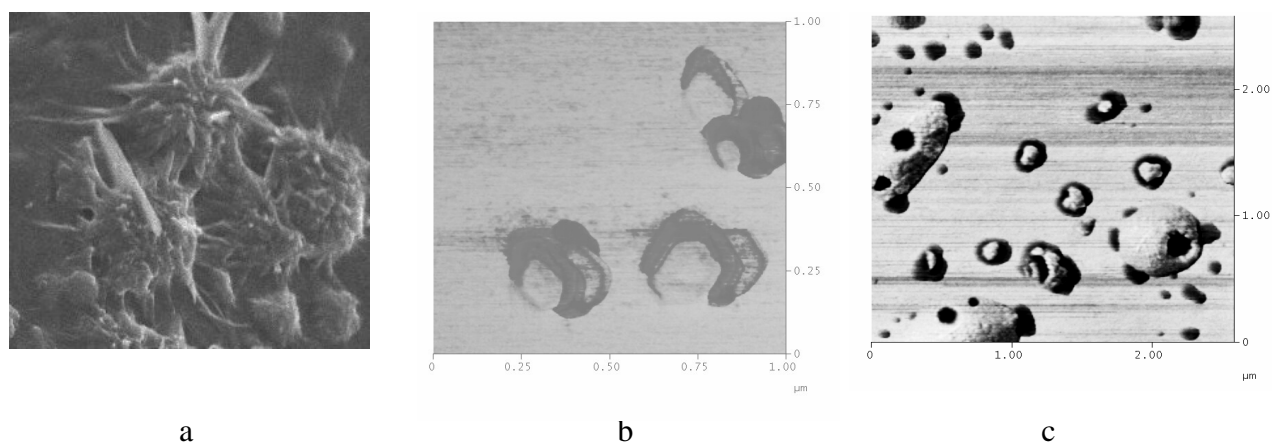


Figure 6. Composite materials developed by RESS
a- PDMSH-TDI; b- FAA-DSP; c-EPA-DSP

Nanocomposite particles were also produced by RESS by coprecipitation from solutions containing multiple solutes. Figure 6b is an AFM phase image of some polymer-monomer RESS coprecipitates. A fluoroalkyl acrylate (FAA) polymer and 2,5-distyrylpyrazine (DSP) monomer were dissolved in a common solvent and coprecipitated in a particulate form. Then the DSP monomer was recrystallized within the FAA polymer phase and polymerized by UV light to ensure stability of the developed structures. Figure 6c depicts an AFM phase image of diethyl p-phenylenediacrylate (EPA)-DSP particles. EPA and DSP monomers were dissolved in a common solvent, precipitated by RESS, and polymerized by UV light. These examples illustrate a promising approach used for the development of novel composite coatings for various sensors.

ACKNOWLEDGEMENTS

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