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Improving the stability of surface acoustic wave (SAW) chemical sensor coatings using photopolymerization

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Abstract

Submicron particles of a diethyl ester of *p*-phenylenediacrylic acid (EPA) were produced by the technique known as rapid expansion of supercritical solutions (RESS) and were deposited onto surface acoustic wave (SAW) resonators. The EPA particles were polymerized in the solid-state directly on the surface of the SAW devices in order to stabilize the mechanical properties of the sensor coatings. The sensor affinity to particular vapors was enhanced by performing the polymerization step in the presence of organic template vapors. The resulting SAW sensors exhibited high quality factors (Q_0) and we have demonstrated the sensor stability for periods up to 3.8 years.

Keywords: Gas sensor; Surface acoustic waves; Photopolymerization; Rapid expansion of supercritical fluids; Coating stability

1. Introduction

Gas-phase chemical sensors based on surface acoustic wave (SAW) devices were first reported more than two decades ago [1]. Current SAW-based chemical sensors employ an array of sensors to detect and identify gas-phase analytes. Each sensor element of the array is coated with a different thin polymer film selected to provide preferential affinity to a specific vapor class based on its polarity, polarizability or ability to participate in hydrogen bonding. The combined output pattern of the array is used to recognize the presence of specific vapors with high reliability and sensitivity [2,3]. The thin polymer film plays the key role for achieving optimum overall sensor performance. For optimum performance, a sensor coating must have strong adhesion to the SAW device surface, should reversibly absorb the analyte vapor and must maintain mechanical integrity over a range of operating conditions and temperatures. Finally, a good coating must be stable over time and resilient to various conditions in the storage and measurement media [4–6]. Highly viscous linear (jelly-like or rubbery) polymer coatings are normally preferred in chemical sensors since they provide high vapor permeability [6]. However, rubbery coatings are susceptible to time-dependent mechanical changes caused by interactions with the surface of the SAW device, resulting in unwanted changes in sensor performance [4,7]. Fig. 1 is an optical microscope image illustrating the morphological changes observed in a methylphenylsilicon polymer (OV-25) coating after 1 h. OV-25 is commonly used for the detection of non-polar aromatic molecules [8]. Initially, the transducer surface is coated with a smooth polymer film, but after 1 h and under standard atmospheric conditions, the coating agglomerates into an ensemble of small droplets. Crosslinking has been proposed as a potential method to prevent these kinds of unwanted morphological changes that are frequently observed in SAW sensor coatings. Unfortunately, it is very challenging to perform chemical reactions on the surface of a SAW device without interfering with the SAW resonance condition [4]. In addition, rigid polymer films were found to exhibit lower vapor sensitivities and are susceptible to fragmentation [4].

Our research group has been investigating the potential advantages of using particulate polymer coatings instead of continuous films on SAW devices. Previously, we demonstrated that particulate coatings can significantly improve the sensitivity of SAW devices by providing a higher surface area for vapor interactions [9]. However, it is well known that particulate coatings can act as scattering centers and interfere with the propagation of acoustic waves, thereby compromising the acoustic resonance condition. The effect of coating morphology

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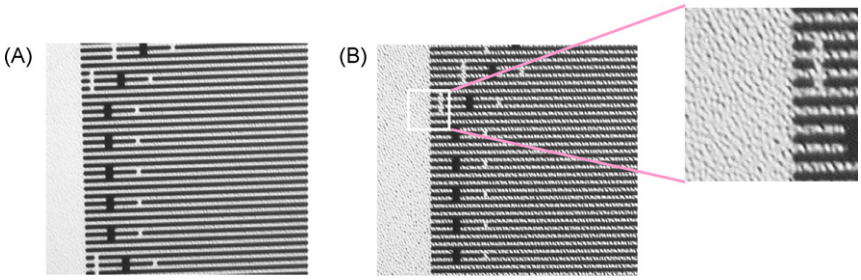

Fig. 1. Film disintegration of OV-25 polymer on the SAW device surface: (A) 5 min after coating and (B) 1 h after coating. The light regions are gold interdigitated electrodes deposited onto the underlying dark quartz substrate.

on device performance can be evaluated by quality factor (Q_0) measurements. The quality factor is a quantitative representation of the sharpness of the resonance curve. In general, SAW devices with a low quality factor have lower sensitivities and are not desirable as chemical sensors [10]. In this paper, we report a method for increasing the stability of SAW coatings without degrading the acoustic resonance condition of the SAW transducer. Submicron polymer particles were deposited and polymerized directly on the SAW device surface, and the resonance condition and vapor affinity of the SAW sensor were monitored over time. It is shown that the vapor affinity of the coating is stable and can be tuned through the introduction of a template vapor during the polymerization step.

2. Experimental

2.1. Materials and equipment

HPLC-grade pentane, hexane, heptane, octane, isooctane, nonane, decane and 1-butanol were obtained from Fisher Scientific. Freon 22 (chlorodifluoromethane) was obtained from DuPont. The diethyl *p*-phenylenediacrylate (EPA) was synthesized using a procedure described previously [11]. Methylphenylsilicon OV-25 was obtained from Sigma–Aldrich. Nitrogen was from National Welders and has grade 5.5. SAW 250 MHz resonators were from Microsensors Systems, Inc. For polymerization of EPA particles, a UV lamp from American Ultraviolet was used. This lamp has 100 W power and emits UV within the range of 325–382 nm. Evaluation of the electrical properties of the SAW devices was performed with an HP 8353 D network analyzer. Unloaded quality factors (Q_0) were calculated with the Qzero computer program developed by Kajfez [12].

2.2. SAW device preparation

2.2.1. Particle development

A schematic representation of the RESS process is depicted in Fig. 2. The solute material (EPA monomer) was dissolved in supercritical Freon 22 in a pressure vessel. The temperature of the pressure vessel was controlled using a tube furnace. The single-phase supercritical solution was expanded through a capillary nozzle into atmospheric conditions, and phase separation occurred as the expanding solution crossed into the two-phase region. Solvent-free submicron EPA monomer particles were precipitated and deposited directly onto the surface of SAW resonators. The coating thickness was carefully controlled and corresponded to a SAW frequency shift of about 400 kHz. A more detailed description of the apparatus and experimental procedure is provided in a previous article [9]. In order to study the morphology and the structure of the monomer and polymer particles, the particulate coatings on the SAW devices were replicated on glass slides and were examined by optical and SEM (JEOL JSM-820) microscopy.

2.2.2. Polymerization of EPA particles

The EPA coatings on the SAW devices and glass slides were polymerized in air and in the presence of 1-butanol vapor, which was chosen as a model template molecule. The SAW devices were placed in a sealed UV-transparent chamber and the chamber was filled either with air or air with saturated template vapor. The chamber was kept in the dark until polymerization initiation. In order to facilitate polymerization, the samples were exposed to UV light for 15 min from a distance of 22 cm. After polymerization, the coatings were flushed with dry nitrogen for 20 min to remove the template.

2.2.3. Sensitivity evaluation

The resulting SAW sensor response was tested upon exposure to analyte vapors at various concentrations using a custom-built sensor testing system. The details of this system were described previously [9]. The system is equipped with a vapor generation unit. This unit produces saturated organic vapors at $10 \pm 0.1\,^{\circ}C$. The organic vapors are diluted with nitrogen and delivered to a pair of SAW devices at a constant temperature of $30\,^{\circ}C$. The pair of SAW devices includes one reference device and one coated device, and the frequency difference is measured. The reference device is uncoated and is exposed to pure nitrogen at the same flow rate and temperature as the analyte stream directed to the

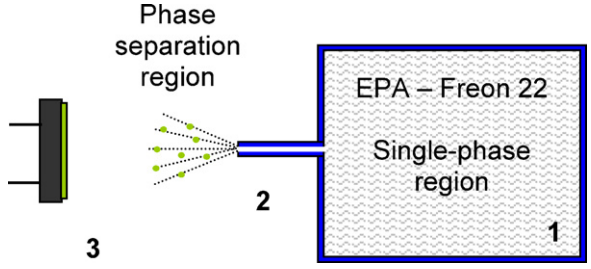

Fig. 2. Schematic representation of the RESS process: (1) high pressure vessel with the supercritical solution, (2) capillary nozzle and (3) SAW transducer.