A FOREST WITHOUT TREES: DEVELOPMENT OF HIGH-SURFACE-AREA MATERIALS FOR ENHANCED-SENSITIVITY SAW ARRAY

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INTRODUCTION

Chemical sensor arrays are an alternative to the tedious development of highly specific single-analyte detectors [1]. Our recent efforts have focused on the chemical and physical diversity of interface materials for SAW sensor arrays [2]. However, the issues of wide dynamic range and high sensitivity must also be addressed for sensor arrays to compete in applications requiring low detection limits. Because SAW devices respond in proportion to change in mass per nominal unit area of the device surface, sensitivity is enhanced by surface modification with high-area, thin-film coating materials: a greater mass of analyte is adsorbed at a given ambient concentration.

We are exploring several classes of electrochemically prepared high-area films, materials whose formulations and processing are well documented [3] for applications other than chemical sensors. We present results from films formed by anodization, chemical conversion, and electroplating, yielding surface area enhancements as high as 170x.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows three high-area coating materials, each with a unique morphology. Figure 1a shows the leafy crystal morphology of copper oxide formed by chemical conversion of 400 nm of evaporated copper using potassium persulfate. Figure 1b reveals a highly dendritic coating of platinum "black," electroplated from chloroplatinic acid laced with lead acetate. Figure 1c is a porous Al_2O_3 film formed from an evaporated Al film under fixed DC potential in dilute phosphoric acid. Not shown but also studied were Al_2O_3 films formed by anodization in sulfuric and oxalic acids, as well as cathodically deposited "black" (high area) films of Pd, Au, Ni, and Cr [3].

To determine film surface areas, we recorded *in-situ* nitrogen adsorption isotherms at 77 K in a variant of the BET technique developed specifically to characterize thin films on SAW devices [4]. Figure 2 shows such an isotherm for a Pd black film, one of the materials with which we most consistently obtained high area enhancements. The area enhancements calculated from the N_2 isotherm, along with the mass/area of N_2 adsorbed at $p/p_{\text{sat}} = 90\%$, are summarized in Table 1 for a number of films.

A factor limiting surface area enhancement is attenuation of the SAW by the high-area films. Thick, dense films attenuate the SAW, and feature sizes comparable to (or a significant fraction of) the 32 μm acoustic wavelength scatter the waves, causing further attenuation. In practice, coating feature sizes are typically much smaller than 32 μm (Figure 1), so film mass/area is the primary limitation. Thus, we achieved significantly better results (thicker usable films) with black Pd than with black Pt or Au, which have almost twice the density of Pd. Lower density materials such as black Cr should be better still, and the exceptionally low density of porous Al_2O_3 ought to be best. For these materials, however, we have had difficulty in producing high-area, open-pore structures with as much accessible surface area as the Pd black.

To evaluate the sensitivity and selectivity of the electrochemically formed films, we recorded adsorption isotherms from 18 analytes [1] over the 0.1 – 80% of p_{sat} range using arrays of 6 high-area film-coated SAW devices (devices and test system described in [1,2,4]). The *n*-propanol and *i*-octane isotherms of Figure 3 typify the response enhancement due to surface mass loading on the high-area coatings: the signal is 50 – 60 times larger for the copper oxide-coated device at $p/p_{\text{sat}} = 50\%$ than for the uncoated reference. Parameters found to influence the extent of enhancement include coating thickness and density, the potentials used to apply and process the films, and, importantly, details of the "seed" substrate layers upon which these films are formed.

Table 1. BET surface areas obtained from 77 K N_2 adsorption isotherms of electrochemically formed films on SAW devices.

Coating (thickness, nm)	Surface Area Enhancement	Max. N_2 ($\mu\text{g}/\text{cm}^2$)
Pd black	173	17
CuO conversion (1450)	50	4.6
Cr black	42	6.2
Pt black (390)	41	2.4
Au black (530)	22	1.5
Ni black	20	1.7
Al_2O_3 from $\text{H}_2\text{C}_2\text{O}_4$ (300)	19	2.8
Al_2O_3 from H_3PO_4 (210)	4.0	0.6
Al_2O_3 from H_2SO_4 (130)	3.7	9.2
Au seed layer (20)	2.8	5.5
Bare quartz	0.9	0.2

CONCLUSIONS

By enhancing SAW device surface area, detection limits can be improved by a factor of at least 100. We are using the chemical diversity of the high-area materials reported here, as well as further chemical modification of these films, to achieve the chemical diversity necessary to develop a multielement array of high-sensitivity SAW sensors.

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Figure 1. Scanning electron micrographs of (a) copper oxide, (b) black Pt, and (c) anodized Al thin films. The scale bar at the lower right of each panel is 600 nm long; all three panels are shown at the same magnification.

Figure 2. SAW-measured N_2 adsorption isotherms at 77 K from one bare and three high-area film-coated SAW devices. A one ppm frequency shift is equivalent to a 97 Hz frequency change for these 97-MHz ST-quartz delay lines. Increased mass loading causes negative shifts in oscillation frequency.

Figure 3. Adsorption isotherms of *n*-propanol and isooctane on one bare and three high-area film-coated SAW devices.