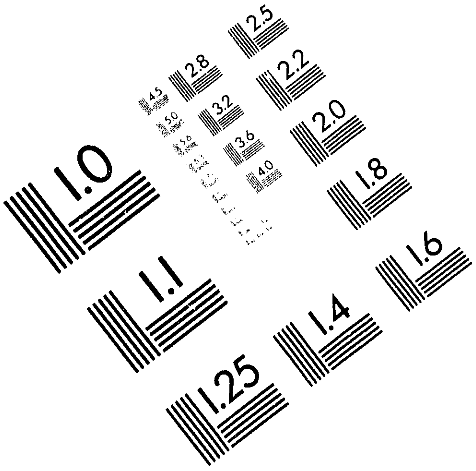

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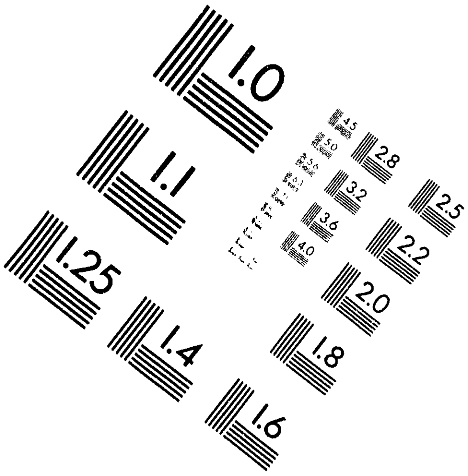

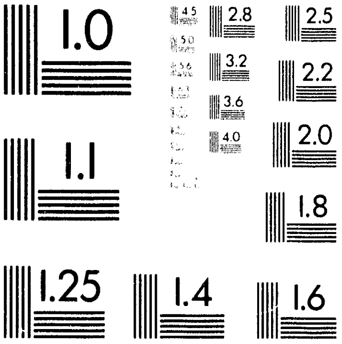

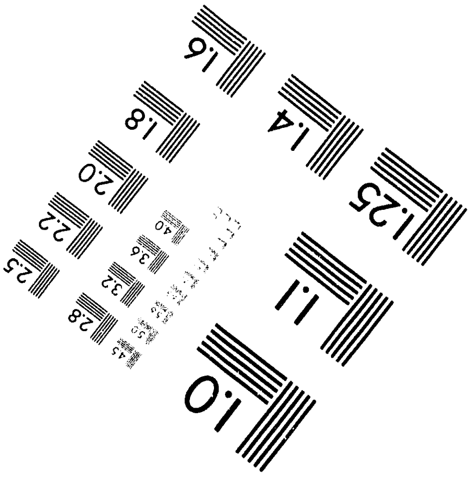

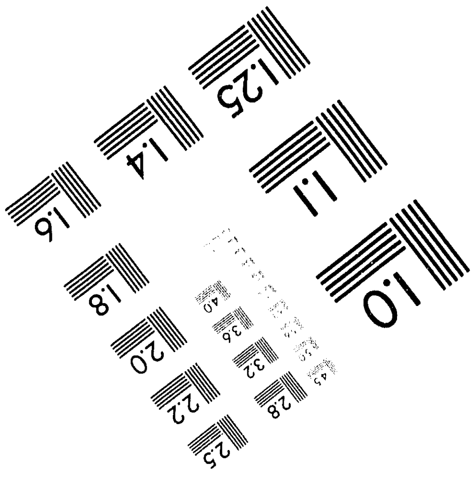

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SAW Chemical Sensor Arrays using New Thin-Film Materials[†]

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Abstract

We have used two classes of materials, self-assembled monolayers (SAMs) and plasma-grafted films (PGFs), as new chemically sensitive layers for an array of 97-MHz surface acoustic wave (SAW) delay-line-based devices. The responses of these materials to each of 14 different analytes, representing the classes of saturated alkane, aromatic hydrocarbon, chlorinated hydrocarbon, alcohol, ketone, organophosphonate, and water, have been evaluated using our six-SAW device array. The results reveal a qualitative "chemical orthogonality" of the films that is very promising for pattern recognition analysis.

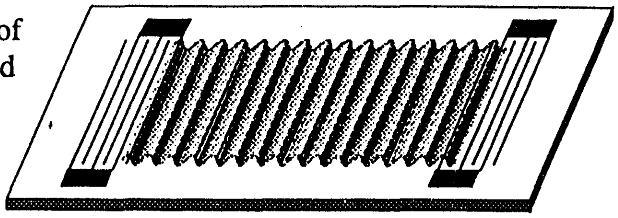

Figure 1. SAW device showing propagating acoustic wave; chemically sensitive coating occupies the region between transducers.

Chemical sensor arrays offer the promise of selective chemical detection without the need for perfectly chemically selective thin films. Nevertheless, the chosen array of films must have a significant degree of "chemical orthogonality"—preferential response to different classes of chemicals by each of the different films—for the maximum amount of information to be obtained from the array response [1]. To this end, we are exploring two relatively new classes of thin film as a means to expand the range of usable coating materials: self-assembling monolayers (SAMs) and plasma-grafted polymer films (PGFs). These films are very thin, ranging from a single molecular layer to 100 nm, so a sensor platform with relatively high sensitivity is required to provide response over a useful range of analyte concentrations.

Surface acoustic wave (SAW) devices respond to very small surface mass changes (< 100 pg/cm^2) and to a range of other perturbations [2,3]. The potential for enhanced signal-to-noise ratios and lower insertion loss using the SAW resonator has led to a recent increase in its popularity for chemical sensing applications [4]; nevertheless, the SAW delay line, shown schematically in Figure 1, retains some important advantages. Problems with resonators for chemical sensing applications include a very nonuniform distribution of acoustic energy (and hence mass sensitivity) over the active sensing area of the device; the presence of a reflector array, which creates a large number of steps on the device surface that may act as preferential adsorption sites (most likely to be a problem for very thin sensing films); susceptibility to complete damping of the acoustic resonance by a lossy sensing film; and, if the chemically sensitive material is conductive, the need to pattern the film into two or even three separate

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[†] Proceedings for the 5th International Meeting on Chemical Sensors, Rome, Italy, July 11 - 14, 1994.

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regions to avoid shorting the interdigital transducers, as opposed to one easily patterned interaction region in the case of the delay line.

We have designed and constructed a six-SAW device array fixture and associated instrumentation that allow simultaneous measurement of changes in both SAW velocity (*via* oscillation frequency) and SAW attenuation (*via* insertion loss) of six 97-MHz ST-quartz SAW delay lines (for which fabrication details are reported elsewhere [2]), each bearing a different chemically sensitive layer. Using our gas flow system [5], a N_2-entrained stream of the analyte is delivered in parallel to all six of the devices. Each delay line is operated in an oscillator loop configuration as detailed elsewhere [2], with an RF multiplexer (HP 3488A/44478A) used to connect each oscillator loop in sequence to a single frequency counter and vector voltmeter for measurement of oscillation frequency and insertion loss, respectively. One measurement cycle, in which all six frequencies and insertion losses are recorded, requires approximately 15 s to complete, limited primarily by the 1 s counter gate time.

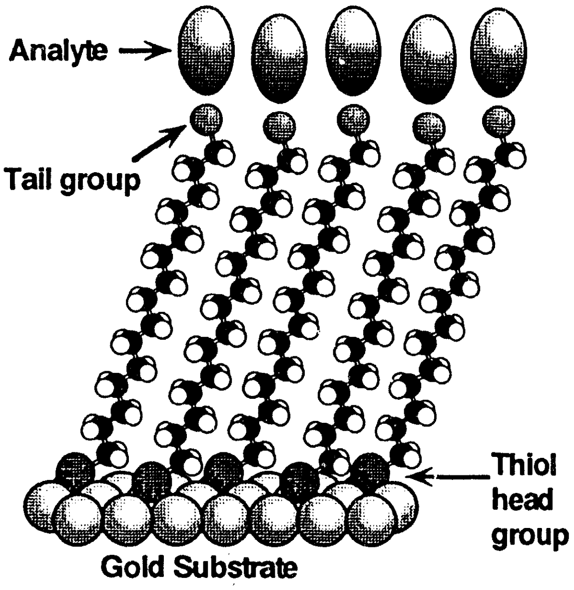

Figure 2. Schematic of interaction between self-assembled monolayer and analyte.

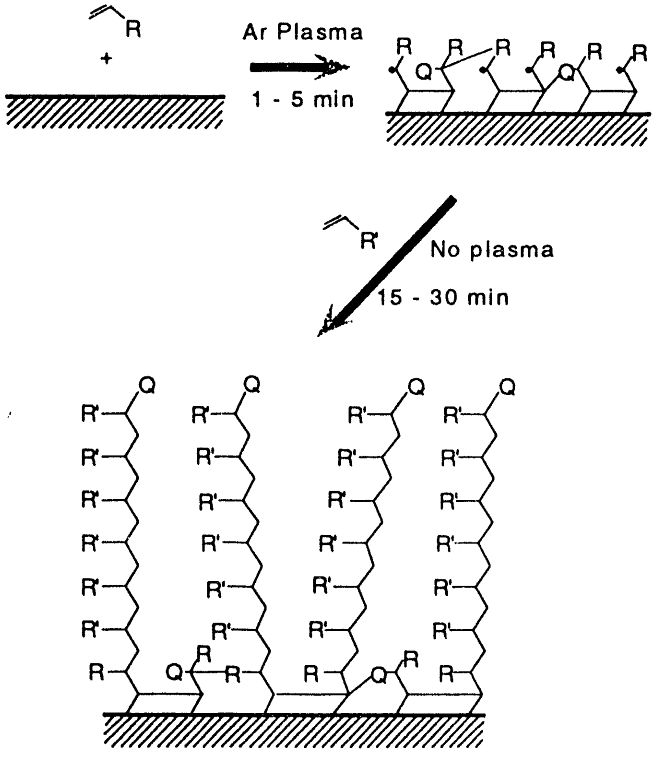

Figure 3. Formation of plasma-grafted film. Q is a free-radical quencher.

SAMs are formed by a combination of a strong chemical interaction between a head group and a substrate, plus the cumulative van der Waals interactions between hydrocarbon tails of adjacent molecules; the SAMs we have studied all utilize thiol (SH) head groups interacting with a gold film substrate that is thermally evaporated onto the interaction region of each SAW delay line [6]. The result is a highly ordered, one-monolayer-thick film that is essentially in epitaxial registry with surface sites on the substrate. The interaction of a SAM with an analyte is shown schematically in Figure 2.

Plasma-grafted films are a relatively little-explored form of polymer [7] with the potential to incorporate a wide range of functional groups in a very open, permeable matrix. The process of plasma grafting is outlined in Figure 3. The resulting thin "base layer" is highly crosslinked, but the grafted layer has an open, "kelp forest-like" structure. Such films *do not* have the ordered nature of SAMs, but do allow the incorporation of many different functional groups into a highly permeable thin film.

We have obtained sensor responses for Au-coated delay lines functionalized with SAMs of $HS(CH_2)_{15}CH_3$; $HS(CH_2)_{10}COOH$; and $HS(CH_2)_{10}COO^-$ coordinated to various transition-metal ions, including Cu^{2+}, Ni^{2+}, and Fe^{2+}. We have also obtained responses for SAW devices (without gold films) coated with several PGFs, including acrylic acid, vinylphosphonic acid, and eugenol.

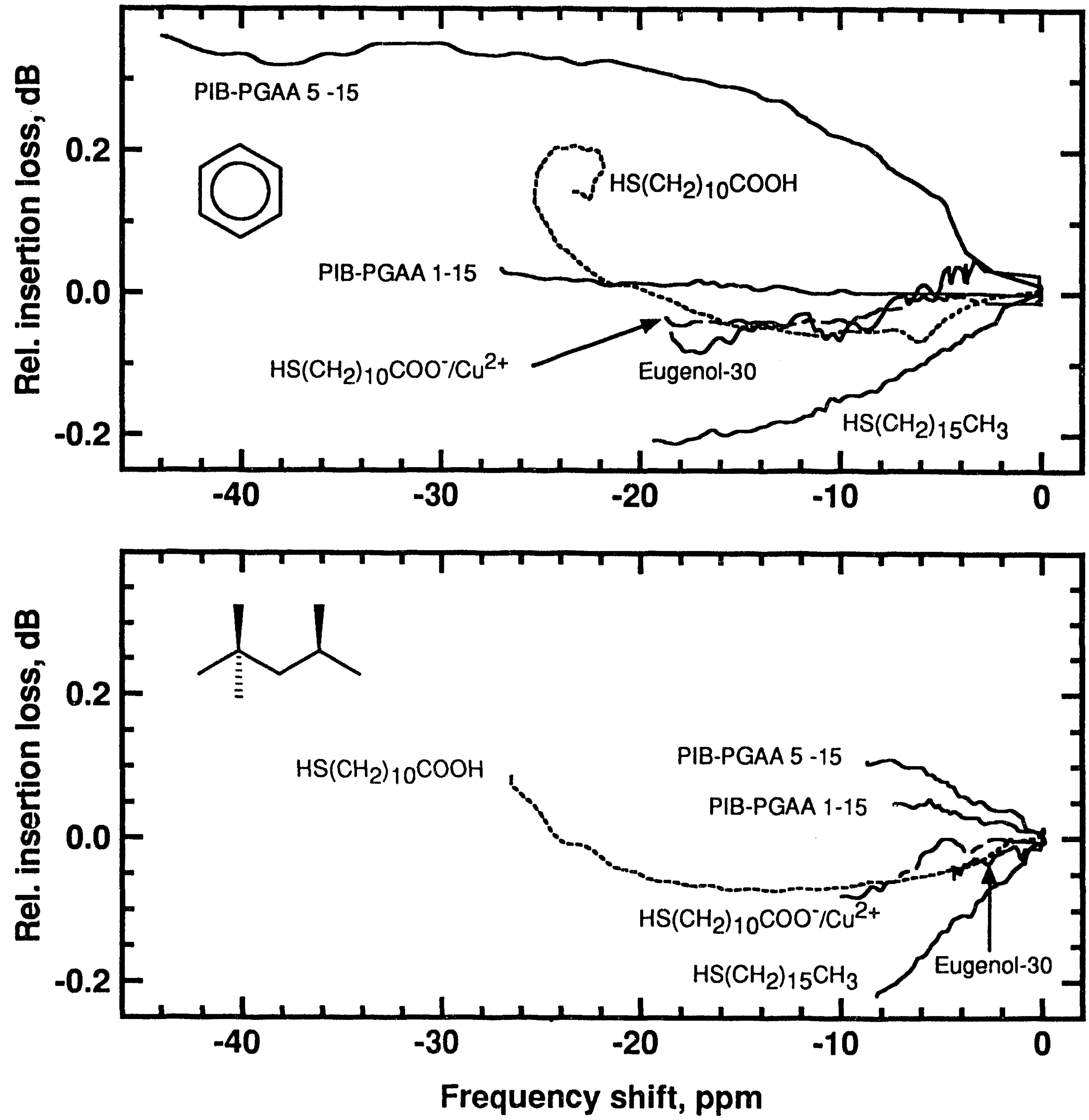

Figure 4. Insertion-loss-change-vs.-frequency-shift isotherms for benzene (top) and i-octane (bottom) exposure of six-SAW device array. The origin corresponds to $p/p_{sat} = 0$ and the distal ends of the curves to $p/p_{sat} = 0.5$. PIB is poly(isobutylene); PGAA is plasma-grafted acrylic acid.

The arrays of SAW devices were exposed to a number of volatile organic compounds, including DIMP (diisopropylmethylphosphonate), DMMP (dimethylmethylphosphonate), CCl_4, trichloroethylene, acetone, methanol, *n*-propanol, pinacolyl alcohol, benzene, toluene, *n*-hexane, cyclohexane, and *i*-octane, as well as water. In every case, a four-hour adsorption/desorption isotherm was obtained by slowly ramping the concentration of the organic vapor in a nitrogen carrier stream from 3% to 50% of its saturation vapor pressure and back to 3% again. Over the course of this isotherm, frequency-shift and insertion loss data were obtained for each of the coated SAW devices.

Two such sets of isotherms are shown in Figure 4 for exposure of six SAW devices to benzene and *i*-octane. The isotherms are plotted with change in SAW frequency on the horizontal axis and change in attenuation on the vertical axis; analyte concentration is the variable parameter as each curve is traversed from the origin. For each concentration of solvent, there is a corresponding set of 12 points: six frequency shifts and six attenuation changes. Such plots vary significantly in "general appearance" from one analyte to the next, even for the two hydrocarbon solvents shown. We are in the process of applying multivariate cluster analysis techniques to these data, with very promising preliminary results.

Acknowledgments

Helpful technical discussions, and collaboration on the design of the six-device array fixture by Stephen J. Martin of Sandia National Laboratories (SNL) are gratefully acknowledged, as is the excellent technical assistance of A. W. Staton, M. Hill, and M.-A. Mitchell, all of SNL. This work was supported by the U.S. DOE under contract DE-AC04-94AL85000.

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