Design and Characterization of Selectively Permeable Thin-Film Coatings for the Detection of Volatile Organic Compounds

A Proposal

by

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I. Introduction

Chemical sensing of vapor-phase analytes is a diverse analytical problem which ranges from routine quality-control analysis to field-sensing of analytes within dynamic environments. Central to all of these analyses is the issue of signal transduction, the conversion of a chemical presence to a measurable physical property such as a voltage, current or frequency shift. Vapor-phase sensing of analytes retains the majority of challenges present in solution-based analysis with the addition of several medium-specific obstacles such as a lack of conductivity, limited solubility, thermal susceptibility, difficult containment, low analyte concentrations and the inability to use biological-type recognition approaches. It is because of these gas-phase limitations that the transducer selection must be carefully evaluated. One such device which offers adequate sensitivity to detect the limited quantities of analytes typically present in vapor-phase samples is the surface acoustic wave (SAW) sensor. Functioning as a nanogravimetric sensor, the SAW device is capable of measuring changes in the mass of analyte present in a flowing gas stream due to interfacial adsorption and/or desorption. In addition to this quantitative measurement, it is often of significant interest to also ascertain qualitative information about the species being detected. Such goals may be accomplished by devising an array of sensors which can be 'trained' to recognize individual analytes by their cumulative response on several sensors simultaneously. However, this approach necessitates the development of various sensors with differing chemical selectivity. Surface modification of SAW devices with a variety of thin film coatings, ranging from monolayers to polymeric films, can be tailored to offer varying analyte adsorption/desorption characteristics.

Of interest in my research is the ability to attach dendrimers to substrate surfaces and utilize their porous nature to mediate access to the underlying substrate surface. Previous research in our group has investigated the applicability of dendrimers to chemical sensing and to chemical permeability in homogeneous solution environments and on substrate surfaces utilizing surface-confined dendrimers. My focus will be on the development of tailored chemically selective thin-film coatings for the analysis of volatile organic compounds. Specifically, I intend to use dendrimers and dendrimer/polymer (Gantrez) thin films atop SAW device sensors to enhance chemical selectivity via 'trans-dendrimer' analyte filtration. In addition to tailoring chemical selectivity I will simultaneously work to enhance the sensitivity by incorporating high-surface-area alumina SAW devices through a collaborative effort with Sandia National Labs. My preliminary results have illustrated a greatly enhanced chemical response from the high-surface-area SAW devices in comparison to traditional planar devices along with thin-film selectivity which can mediate access to the substructure of the devices. Additional tailoring of the thin-film composition will be directed towards enhancing the selectivity and analyte specificity.

II. Background

Thin-films on SAW Devices

The incorporation of thin-films atop surface-acoustic-wave devices has been investigated by researchers as a means to achieve two primary goals: enhance chemical selectivity and sensitivity. While it may be feasible to tailor the film composition to achieve greater selectivity, the attainment of enhanced sensitivity is typically derived by utilizing films of increasing thickness, which ultimately reduces the device's limit of detection as reported by Göpel and co-workers. [1] This competition between maximizing both the selectivity and the sensitivity underscores the care which must be taken in the application of thin-film coatings upon SAW devices if the film is to be a beneficial addition to the technique. To this end, my research will be focused on utilizing the thin-film strictly as a selectivity-agent and allow the specialized high-surface-area substrate material to enhance the sensitivity compared to traditional planar SAW devices. A general rule-of-thumb for polymeric film coatings on SAW devices is that to minimize negative effects, such as resonance attenuation, the film thickness should not exceed a value of 1% of the Rayleigh-wave wavelength. As will be discussed later in this proposal, we plan to use devices that oscillate at a nominal 97 MHz on ST-cut quartz substrates yielding a wavelength of 32 μm. The polymeric films described here have an ellipsometric thickness of approximately 20 nm, which is well below the thin-film limit.

While SAW sensors ideally operate as purely nanogravimetric devices, measuring only changes in mass loading upon their interfacial surface, in reality the signal is a complex combination of variables such as temperature, mass, pressure and film rigidity. In addition to the effect these variables exert upon the SAW device, the presence of the accompanying thin-film and it's susceptibility to these variables must also be considered. Under typical experimental conditions with a bare (unmodified) SAW device, these variables are minimized by active thermal controls, constant gas flow rates and use of moisture-free purge gases. These defined parameters diminish the effect of the non-analyte contribution to the observed signal. In addition to these concerns, a thin-film modified SAW device still must contend with the possibility of detrimental interactions between the analyte and the polymeric coating. Analyte compatibility in the case of coated-SAW sensors extends beyond the traditional concerns of decomposition, miscibility and complexation.

Since the acoustic Rayleigh wave propagates across the surface of the device, and consequently through the entirety of the film, the density of the film (rigidity) is a critical variable throughout the course of an experiment. This film 'rigidity' is termed the viscoelastic modulus of the coating. Any changes in this property during the course of an experiment may be inadvertently attributed as an analyte response since these changes in 'density' will affect the velocity of the acoustic wave through the medium and thus the observed frequency shift. [2-5] These changes arise from 'stiffening' or 'softening' of the polymeric film due to interactions with the adsorbed analytes. In the case of non-reversible analyte adsorption, the continual accumulation of mass within the polymer can erode the expected sensitivity of the film. [6] By limiting the thickness of the film, any modulus change induced by an interaction with the analytes will be minimal in comparison to the bulk of the wave propagating in the quartz substrate. It is well known that temperature also affects the density of materials and thus the velocity of an acoustic wave traveling through these materials, this applies to film as well as the substrate. Zellers and co-workers have performed extensive research on temperature and humidity effects on polymer-coated SAW devices observing that changes as small as 0.1 ˚C can induce significant errors due to baseline shifts. [7] In addition to using a temperature-regulated flow-cell, my research also utilizes a specific cut of quartz (ST-cut) which provides a near zero temperature coefficient at values nears room temperature.

When all of the variables that contribute to SAW performance are appropriately balanced, it is possible for acoustic-wave-based sensors to exhibit extraordinary selectivity, such as distinguishing between n-octane and iso-octane. [8]

Dendrimeric Polymers

Poly(amidoamine) (PAMAM) dendrimers [9] are macromolecules that exhibit repetitive three-dimensional branching outward from a central ethylenediamine core. This ‘tree-like’ branching structure is established by sequential substitution of amidoamine units. Figure 3 illustrates a fourth-generation amine-terminated PAMAM dendrimer (G4-NH_2). Iterative addition of branches results in an increase in size (diameter) and due to increasing steric crowding of the terminal groups, the dendrimers develop more three-dimensional structure. These sequential stages of growth are referred to as ‘generations’ since each previous modification gives rise the subsequent addition. The novel nature of discrete spheroid monodisperse polymers has attracted great interest from the chemical community and researchers have investigated applications in the fields of drug-delivery, host-guest chemistry and catalysis. [10] Initial experiments have been performed with the covalent attachment of dendrimers to planar substrates.[11] Additionally, the permeability of surface-confined dendrimers has been studied in solution where they have been found to act as molecule-sized gates to mediate surface accessibility. [12] Preliminary studies of dendrimers have been performed on planar-substrate SAW devices to investigate their interactions with various volatile organic species. [13] My research will be based on using dendrimeric films as vapor-phase gates or ‘filters’ to effect selective permeability across the substrate surface.

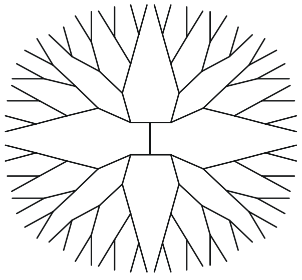


Figure 3: G4 PAMAM Dendrimer

Branches = $-N(CH_2CH_2CONHCH_2CH_2N-)_2$

Terminal End Groups = $-NH_2$ or $-OH$

Gantrez Polymer

My preliminary results indicate that high-surface-area alumina SAW devices modified with G4-NH_2 offer insufficient selectivity between volatile organic compounds. As will be discussed in detail later, this result is attributed to the variability in the pore size of the porous alumina substrate. However, secondary modification of the surface-confined dendrimers with Gantrez, poly(maleic anhydride)-*c*-poly(methyl vinyl ether), (Figure 4) offers a route to minimally increase the film thickness while simultaneously expanding the available surface chemistry to alternative cross-linking pathways. [14] After addition of Gantrez to the dendrimers it will be possible to incorporate additional dendrimers or cross-linkers *within* the polymeric film to selectively pass analytes to the underlying substrate. This approach offers the benefit of bridging any pores not previously capped by the dendrimeric monolayer and the nature of the cross-linking agents (dendrimers, diamines, diols…) can be selected to simultaneously affect chemical selectivity. Gantrez permeability has been shown to be affected not only by covalent cross-linking but also by thermally-induced cross-linking. [15] I propose to utilize all of these properties of the Gantrez polymer to my advantage in fabricating thin-films atop porous high-surface-area-alumina SAW devices as a method to mediate access to the substructure.

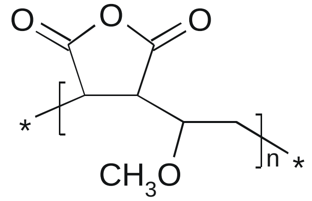


Figure 4: Gantrez (Gz) monomer unit (n= ca. 400)

III. Materials and Techniques

Substrates

I will use two different base materials for my studies, silicon and quartz. Si (100) wafers will be used as the base substrate for planar non-SAW studies such as external reflectance IR (FTIR-ERS), ellipsometry and contact angle goniometry. Onto these Si wafers will be deposited 200 nm of Au or Al via electron beam with an intermediate 10 nm Ti adhesion layer utilized on the Au wafers. Additionally, Sandia National Labs will provide non-anodized planar Al-coated Si wafers henceforth referred to as SNL-Al wafers with nominally identical metalization thickness. The SNL-Al coatings have been thermally deposited onto temperature-controlled wafers held at 0.4 T_m in order to induce enhanced columnar grain structure.

The second set of substrates, the SAW devices, will all be fabricated on ST-cut quartz wafers. While many other materials exhibit piezoelectric characteristics suitable for SAW substrates, quartz is favored because of its lower temperature-coefficient at room temperature. The appropriate ‘cut’ of quartz for use as SAW substrates is known as ST-cut and exhibits the lowest temperature dependence of all the ‘compensated’ quartz cuts along with an acoustic propagation velocity of 3158 m/s. All of the SAW device sensors have the Au interdigitated transducers (IDTs) lithographically deposited with 200 nm of Au atop 10 nm of Ti. The central sensor pad on the devices consist of either 200 nm Au/10 nm Ti, 500 nm SNL-Al or 500 nm of anodized high-surface-area alumina (HSA-Al). Figure 5 is a cross-sectional SEM view of the porous columnar nature of the HSA-Al material atop the quartz substrate. [16]

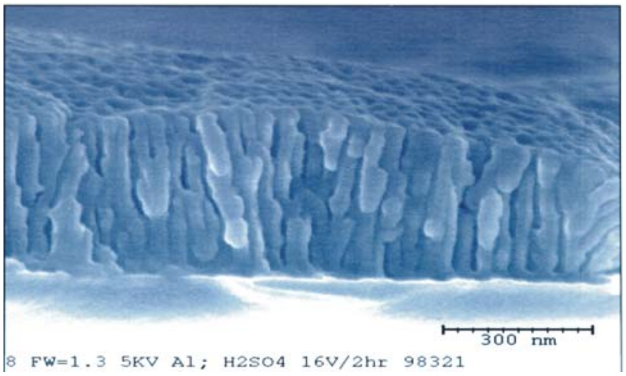


Figure 5: FE-SEM of an anodized Al film which was evaporated on a quartz substrate

Techniques

Surface Acoustic Wave Sensors operate on the principle of the piezoelectric effect, wherein certain crystalline materials can produce a voltage when placed under mechanical stress. Conversely they can undergo physical deformation when an electric field is applied to the crystal. Unlike the more familiar quartz resonators, such as quartz crystal microbalances (QCM), which are also piezoelectrically active but undergo thickness shear-mode (TSM) deformation, SAW sensors undergo surface-confined distortions. Upon application of an oscillatory potential a Rayleigh wave is generated and propagates across the surface of the quartz. White and Voltmer[17] were the first to report the formation of these ‘surface elastic waves’. Up to this point potentials had been applied through the bulk quartz substrates but no method existed for the application of a potential exclusively to the quartz surface. With the advent of the interdigitated transducer (IDT) by lithographically depositing aluminum ‘fingers’ on the quartz surface, researchers focused on electronic signal processing applications. Wohltjen and Dessy later proposed applications of this device to vapor sensing. [18]

Figure 6 schematically illustrates the components of a modern SAW sensor. In practice, the device operates by oscillating at a predetermined frequency, 97MHz in our case, with the

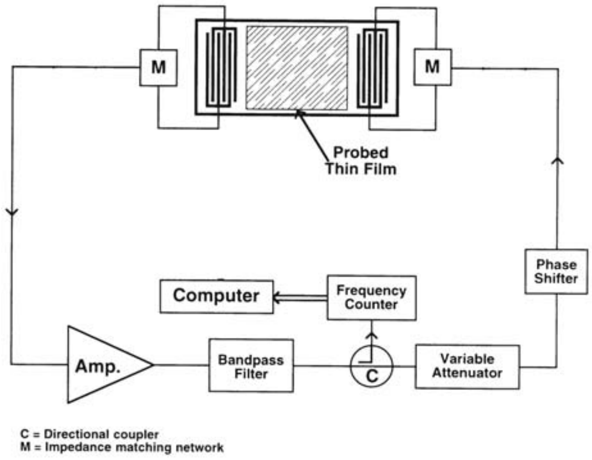


Figure 6: Two-port AW delay line-based oscillator loop illustrating components

quartz oscillator contained within a flowing stream of analyte. As analytes adsorb to the surface of the quartz the mass change causes the oscillation to become damped in accordance with the following abbreviated equation:

$$\Delta f \cdot c_m = \Delta m/A$$

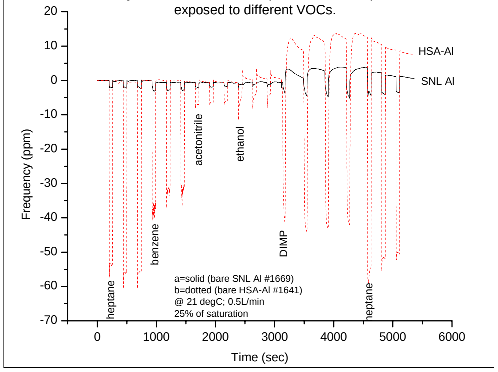
where Δf is the observed change in oscillation frequency caused by the analyte adsorption, Δm is the net change in surface mass due to adsorption, A is the geometric area of the sensor region and c_m is a grouping of constants specific to the design dimensions and properties of the SAW device.

During the course of the dosing experiment the resonant frequency is recorded in real-time via a frequency counter, and the observed frequency shift makes it possible to quantify the mass of adsorbed analyte. The power of this technique as an analytical tool is its inherent sensitivity of measuring nanograms of adsorbed material per square centimeter of sensor area.

IV. Preliminary Experiments

In the initial stages of these experiments I was predominately interested in determining: 1) whether the HSA-Al SAW devices yield larger mass-loading signals when exposed to VOCs than planar Al and 2) whether we can successfully migrate our dendrimer modification techniques from Au substrates to Al devices. Our ultimate goals are to use the high-surface-area devices to improve the sensitivity of chemically-modified SAW devices and to determine if dendrimers can be used as selective nanofilters that can be placed over the pores of the anodized Al substrates (Figure5).

Figure 7: SAW Profile of a)bare SNL Al & b)bare HSA-Al, exposed to different VOCs.



The SAW profiles shown in Figure 7 clearly illustrate the larger mass-loading response of the high-surface-area Al device in comparison to the planar Al device. In previous experiments we had compared HSA-Al SAW devices with planar Au SAW devices and observed similar results, which we attributed solely to surface area differences despite their differences in surface chemistry. The recent availability of planar Al SAW (SNL-Al) devices for these experiments has allowed us to remove the surface chemistry differences and further encourages the previous surface area interpretation. It is worth noting that for the various VOCs utilized, the anodized Al and planar Al devices exhibited similar reversibility characteristics with responses that vary in magnitude but not in profile.

The ability to modify the high-surface-area Al devices with dendrimers is a critical component of our sensor goals. Figure 8 shows an FTIR-ERS spectra of a fourth generation PAMAM dendrimer-modified SNL-Al substrate which used, to model the adhesion of dendrimers on the HSA-Al (HSA substrates are not conducive to reflectance studies). The characteristic dendrimer amide I & II peaks were found to be present on both the 'reference' Au and the SNL-Al substrates. Additionally, ellipsometric measurements show a comparable film thickness on the SNL-Al wafer and the Au 'reference' wafer.

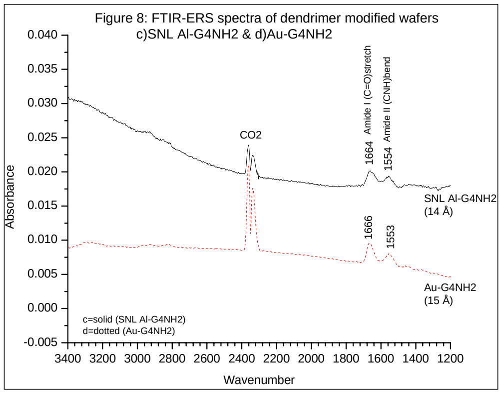


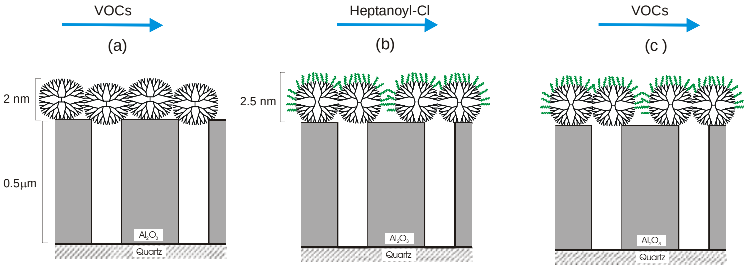
Figure 8: FTIR-ERS spectra of dendrimer modified wafers c)SNL Al-G4NH2 & d)Au-G4NH2

After confirming that I could attach dendrimers to the SNL-Al substrates I began a series of experiments attempting to bridge the HSA-Al pore apertures with dendrimeric films. In comparison to reference Au planar SAW devices the dendrimer-capped devices continued to yield mass loading signals indicating that a large fraction of the analyte was penetrating the dendrimers and accessing the porous substructure. Ultimately we have attributed this 'leakage' to the polydispersity of the substrate pores and consequently incomplete capping of at least some of the pores, which are larger than the selected dendrimers.

In an effort to resolve this problem I performed an in-situ secondary modification of the surface-confined dendrimers with vapor-phase heptanoyl-chloride (Hep-Cl). This was performed to increase the effective bridging-diameter of the dendrimer, alter their hydrophobicity/hydrophilicity and to determine: 1) whether a dendrimer-modified SAW device (planar-or-HSA) experiences a change in sensitivity/selectivity for various VOCs following modification with Hep-Cl, 2) whether such control of periphery group functionality can be exploited to our advantage in future development of selective films and 3) whether it would be feasible to quantify the surface-concentration of dendrimers by measuring the irreversible adsorption of a reactive vapor-phase species.

The process illustrated in Scheme 1 builds upon work previously published in our group[19] utilizing this secondary-modification. It should be noted in the scheme that the dendrimers are specifically illustrated as not entering the porous structure of the alumina. Dendrimers of sufficient diameter (G6) were selected in conjunction with small pore diameter (low anodization voltage) HSA-Al SAW devices in order to approximate the illustrated limiting-case scenario.

Scheme 1:(a) Vapor-phase VOC Dosing of Surface-Confined Dendrimers on HSA-Al SAW Devices
(b) Vapor Phase Functionalization with Heptanoyl-Cl
(c) Effect of Functionalization upon VOC Dosing



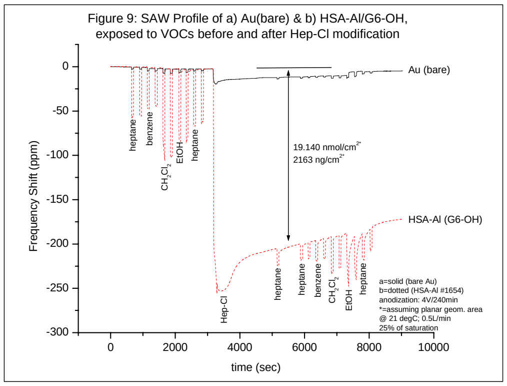
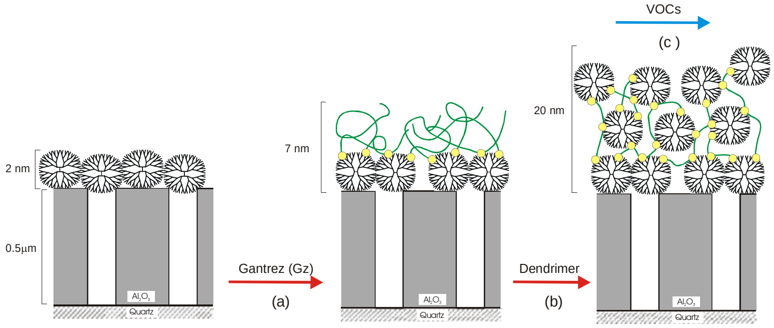


Figure 9: SAW Profile of a) Au(bare) & b) HSA-Al/G6-OH, exposed to VOCs before and after Hep-Cl modification

Additionally, these sequential VOC/Hep-Cl/VOC experiments have been performed to eliminate the necessity of cross-correlating dosant data from HSA-Al devices which may have similar anodization characteristics yet variable surface area.

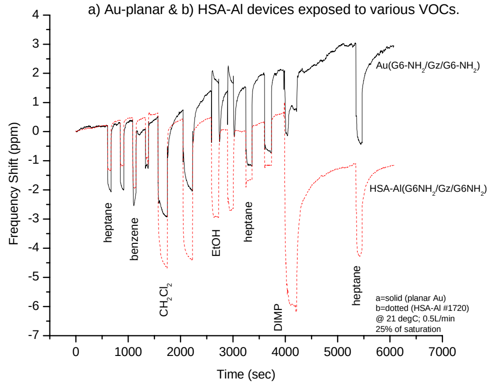
From Figure 9 we observe that the dendrimers alone on the HSA-Al allow appreciable penetration of the VOCs through the pores. This can be seen by the large frequency shifts (>50 ppm) for heptane. Following the irreversible in-situ hep-Cl modification an overall reduction in VOC permeability is observed, ~20 ppm signal response for heptane. However, the planar Au(bare) device exhibits considerable smaller heptane responses, ~3ppm, throughout the experiment indicating that despite the addition of the hep-Cl apparent 'pin-hole' film defects and/or uncovered pores are allowing VOC penetration to the HSA-Al substructure.

Scheme 2:(a) Gantrez Polymer Modification of Surface-Confined Dendrimers on HSA-Al SAW Devices
(b) Secondary Functionalization with Dendrimers
(c) Effect of Functionalization upon VOC Dosing



Incorporation of the Gantrez polymer atop the surface-confined dendrimer has been investigated as an approach to enhance the 'filtering' efficiency of the film in comparison to the results obtained from the dendrimer/hep-Cl film. Scheme 2 illustrates the dendrimer/Gantrez/dendrimer surface modification procedure with is performed ex-situ via solution-phase chemistry prior to introduction in the flow-cell. The application of this procedure, which was previously reported on planar substrates, [14,15] results in a far more impermeable thin-film. We have previously observed mass-loading of heptane on HSA-Al (bare) and HSA-Al/G6-NH_2 with values ≥ 50ppm and for HSA-Al/G6-NH_2/Hep-Cl ≥ 20ppm. This Gantrez modification has resulted in mass-loading of VOCs which are representative of values which we routinely obtain from planar substrates. As illustrated in Figure 10, the mass-loading observed for all the VOCs, except diisopropylmethylphosphonate (DIMP), on the modified Au and HSA-Al are certainly comparable in magnitude. This can be compared to a typical VOC response from HSA-Al, which is about forty times greater than planar Au or planar Al. While it was not our original intent, we have apparently rendered the porous HSA-Al substructure inaccessible to our VOC set.

Figure 10: SAW profile of Dendrimer/Gantrez/Dendrimer modified a) Au-planar & b) HSA-Al devices exposed to various VOCs.



In summary, we have shown that dendrimer-only thin films and dendrimer/hep-Cl films are fully porous to the VOCs, while the dendrimer/Gantrez/dendrimer films are completely non-porous. To achieve our goal of producing selective permeability films we shall seek to tailor an intermediate composition between these two limiting cases.

V. Proposed Research

I propose to implement high-surface-area alumina surface acoustic wave devices as sensing platforms with tailored chemically-sensitive thin-film coatings to improve their sensitivity and selectivity towards volatile organic compounds. Specifically, I plan to investigate the gas/solid interfacial adsorption reactions between dendrimer-only films and composite dendrimer/Gantrez thin-films with vapors of hydrocarbons (aliphatic, aromatic and chlorinated), alcohols and ketones. I also plan to investigate the adsorption characteristics of two nerve-agent simulants; diisopropylmethylphosphonate (DIMP) and dimethylmethylphosphonate (DMMP) on these same composite films as potential chemically-selective vapor-phase organophosphate sensors. To this end, I will utilize these dendrimeric films as nanofilters to mediate access to the underlying porous substrate structure.

To better understand the gas/solid interfacial adsorption reactions occurring on the HSA substrates, I plan to initially characterize their topography, available surface area, kinetic response to analyte dosing, pore-size distribution and the location of the dendrimers on the surface.

In comparison to conventional Au planar-SAW substrates, the SNL-Al and HSA-Al materials interact with the vapor-phase dosants through an interfacial surface of far greater topographic variability. For the unanodized SNL-Al materials, adsorption of the vapor-phase dosants will occur only on the aluminum upper surface, where the surface area is a function of the two-dimensional area and the rms surface roughness. In contrast, the anodized (porous) HSA-Al substrate will interact with analytes in a manner bounded by two limiting-case scenarios: either homogenous surface adsorption along the pore walls and across the upper surface, or adsorption constrained to the upper surface with no analyte entering the pores. The standard conditions utilized in our experiments (vapor concentration, temperature, flow rate) have been selected to rule-out the prospects of ‘capillary condensation’ (vapor-to-liquid transition) of the vapor-phase analytes within the pores. To ascertain an approximate value of the area available along the upper surface, I will perform an atomic force microscopy (AFM) study on all three types of SAW substrates I plan to utilize: planar-Au, SNL-Al and HSA-Al. Certainly, all of these materials are atomically rough and the goal of this series of experiments will be to simply obtain rms surface roughness values for the three materials. The total quantity of surface area available for analyte adsorption is a critical parameter in evaluating the success of our ‘pore-capping’ experiments.

Through the use of in-situ surface modification of the bare Au, SNL-Al or HSA-Al SAW devices, we can determine the quantity of material adsorbed on the surface, and thus the total amount of surface area interacting with the vapor-phase. This pseudo-BET measurement approach can be successfully performed provided the selection of the dosing analytes be constrained to species favored to produce monolayer coatings so that multilayer adsorption will not be mistaken for surface area. For the Au devices, an alkanethiol dosant will be introduced to the flow-cell until a steady-state frequency shift is observed. Following a N_2 purge, the quantity (nmol) of irreversibly adsorbed alkanethiol on the surface can be determined from the frequency shift, which can in-turn be used to extrapolate surface area. [20] Similarly, from observations made in the preliminary results, we have seen that the SNL-Al and HSA-Al devices can be surface-modified via exposure to heptanoyl-chloride. From the observed frequency shift following N_2 purging, the surface area of the porous devices can be obtained. I plan to perform a series of experiments evaluating the quantity of accessible surface area available on HSA-Al devices anodized at varying potentials. The resulting surface area values will be compared to the results obtained by colleagues at Sandia, who are performing similar BET-type measurements utilizing reversible, non-covalent ethanol adsorption.

In addition to understanding the amount of surface available for adsorption at steady-state dosing times, the general time-resolution of our devices is of interest. Of particular interest is the affect the porosity may or may not impart on the adsorption/desorption kinetics. I plan to study the adsorption/desorption kinetics utilizing reversibly adsorbing species, n-alkanes, to answer three questions; 1) Does the porous nature of the anodized devices affect the time-resolution in comparison to planar devices, 2) Is there an observable pore-size dependence on the adsorption/desorption time-scale and 3) What is the lower-limit of response time for these devices to achieve full monolayer adsorption?

One of our primary concerns with the high-surface-area devices is the possible distribution of pore-sizes in two respects; 1) polydispersity of pore apertures on an individual device, 2) varying quantity of surface area between devices which are nominally identical, (same anodization potential). For both cases, the real concern arises from the anomalously large pores which will not be bridgeable by a dendrimeric monolayer. To address this issue, I believe it is important to study the devices and quantify the magnitude of variability. Up to this point, high-resolution field-emission SEM micrographs of the devices have been performed on our behalf by Sandia National Labs at their facilities. While it may be beyond the capabilities of our current university facility to resolve features on the scale of these pores, I believe it is important to my project to continue this characterization. I will get trained on the existing university SEM and attempt to image these pores from an orthogonal and cross-section perspective. The arrival of a new university instrument is pending and may prove more successful at this endeavor, if not imaging will continue at Sandia by their staff or myself. Computational analysis software, NIH-image, will be applied to the resulting images to analyze the pore dimensions and establish their mean and standard deviation. Reports from Sandia on the anodization process have indicated progress toward achieving greater uniformity.

While we specifically select devices of sufficiently low anodization voltage, 2 or 3 V, (nominally 1.5 nm/V) and dendrimers of adequate diameter, (G6 = 6.5 nm) in an attempt to bridge these pores with a dendrimeric monolayer, the need for confirming characterization is obvious. To achieve this goal, it will be necessary to analytically distinguish between dendrimers on the upper surface and those in the pores. Techniques such as SEM and TEM, which offer adequate spatial resolution to image within pores, do not offer the chemical specificity of spectroscopic techniques such as IR, which conversely does not afford adequate spatial resolution. The mean HSA-Al film thickness is approximately 500 nm and the average pore is 5 nm in diameter, far too small for optical approaches. However, I will attempt to utilize confocal microscopy in conjunction with fluorescently-tagged dendrimers to probe this porous film and determine if the dendrimers are entering the pores. This size domain is at the limit of practical resolution for confocal microscopy and it may prove necessary to attempt this series of experiments with thicker Al films (~1000 nm) to provide adequate resolution. While it will not be possible to 'see' any fluorescence within individual pores, a fluorescence eminating from the interior region of the film should provide adequate proof of dendrimer penetration. I plan to approach this problem by performing a study using varying pore-size devices (2V – 16V) and constant-size fluorescent-tagged dendrimer (G6*). By stepping the confocal microscope through the thickness of the Al coating, I will look for fluorescence either exclusively on the surface or throughout the material. A control experiment will be performed with the following structure, HSA-Al/G6/Gantrez/G6* such that the fluorescent dendrimer is prohibited from entering the pores by becoming encapsulated by the Gantrez polymer. At present, the university microscopy center is evaluating confocal instruments for purchase and I hope to perform these experiments with those facilities when they are available. However, other options include borrowing instrument time at the TAMU Vet-Med department or personally performing the experiments at Sandia.

For further investigation of the analyte/film adsorption reactions I will proceed from the point were the preliminary results left off and build layered G6-NH_2/Gantrez thin-films using low-anodization voltage HSA-Al SAW devices. By selecting devices of sufficiently low anodization voltage, 2 or 3 V, (nominally 1.5 nm/V) and dendrimers of adequate diameter, (G6 = 6.5 nm) I will attempt to bridge these pores with a dendrimeric monolayer. Previous results indicate that this pore-capping procedure is not able to fully render the pores inaccessible. High-resolution surface SEM along with cross-sectional SEM images verify the polydispersity of the pore diameters produced by the anodization protocol. It is likely for this reason that the dendrimers are not able to fully passivate the surface since certainly pore apertures exist which are beyond the capabilities of the dendrimers to bridge. Secondary functionalization of the surface-confined G6-NH_2 dendrimers via ester-bond formation with the poly(maleic anhydride)-*c*-poly(methyl vinyl ether) (Gantrez polymer) can be confirmed via FTIR-ERS and ellipsometry. Films of this dendrimer/Gantrez composition have been shown to be VOC permeable while inclusion of a second dendrimer layer *within* the Gantrez yields films impermeable to the VOC set. Through the application of alternative cross-linking agents such as lower-generation dendrimers, diamines or diols I propose to tailor the thin-film characteristics to introduce intermediate VOC permeability. Additional approaches to utilizing monolayer dendrimer films may include direct cross-linking of the surface-confined dendrimers by reaction with diepoxides or an expansion of the heptanoyl-chloride derivatization to use di-functional acid chlorides. These cross-linking reactions will affect permeability by not only cross-linking neighboring dendrimers, but by cross-linking neighboring terminal groups on individual dendrimers. The application of dendrimer-only films is not limited to monolayer deposition; we also intend to evaluate the permeability characteristics of dendrimeric-multilayers deposited by spin-coating methods.

In addition to investigating the VOC response, the composite films will be studied for their chemical selectivity towards organophosphates. The development of a chemically sensitive and specific organophosphate vapor sensor upon a SAW device has been investigated on planar devices, but with the additional sensitivity derived from the HSA material the possibility of lower limits of detection can be investigated. To this end, copper metal ions or nanoparticles can be included within the intra-dendrimer void space or within the dendrimer/Gantrez composite to capitalize on the native affinity of organophosphates to form copper coordination species resulting in extremely sensitive organophosphate sensing platforms.

VI. Summary and Conclusions

I have proposed that chemically selective vapor-phase thin-film sensors composed of dendrimer/Gantrez composite polymers can be incorporated atop porous high-surface-area alumina SAW devices for the effective chemical detection of volatile organic compounds. I have additionally proposed that the composition of the thin-film composite can be tailored to mediate analyte access to the underlying porous alumina substrate.

VI. References

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