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**Single-Monolayer *In-Situ* Modulus Measurements
using a SAW Device:
Photocrosslinking of a Diacetylenic Thiol-Based Monolayer**

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ABSTRACT

We report direct measurement of the modulus change that accompanies the crosslinking of a single molecular monolayer. We measured a change in elastic modulus of 5×10^{10} dyn/cm² as a result of ultraviolet-induced photocrosslinking of a single surface-confined monolayer of the conjugated diacetylenic thiol HS(CH₂)₁₀C≡CC≡C(CH₂)₁₀COOH, designated "DAT" hereafter. The modulus measurement was made on a monolayer of DAT chemisorbed upon a gold film on the surface of a 97-MHz ST-quartz surface acoustic wave delay line. The ratio of the changes recorded in SAW velocity and attenuation, approximately 4:1, suggests that the measured effect is mainly a change in the elastic (real) component of the complex shear modulus, viscous changes playing a lesser role. In relation to typical polymer modulus values, the change of 5×10^{10} dyn/cm² is consistent with a change from a rubbery material ($G' \sim 10^7 - 10^8$ dyn/cm²) to a fairly rigid, glassy material ($G' \sim 10^{10}$ dyn/cm²), reasonable for comparison of the monolayer in its as-adsorbed and crosslinked forms. This report of the direct SAW-based measurement of the modulus change associated with the crosslinking of a single molecular monolayer is complementary to and consistent with previous in-situ measurements of this process using thickness-shear mode resonators.¹

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INTRODUCTION

Film Mechanical Effects Probed with Acoustic Wave Devices

The use of surface acoustic wave (SAW), thickness-shear mode (TSM), flexural plate wave (FPW), acoustic plate mode (APM), and other acoustic wave devices to monitor changes in thin-film mechanical properties has been reported by a number of researchers.¹⁻²² Crosslinking and solubilization reactions have been monitored in photoresists;²⁻³ melting and glass-to-rubber transition temperatures have been recorded for polymer films;⁴⁻²¹ the temperature dependence of the polymer film complex shear modulus has been characterized;^{4,17,22} and plasticization of polymer films due to absorption of organic solvents has been reported.^{4,7,17-21}

In the realm of acoustic wave-based chemical sensors, the consequences of changes in thin-film mechanical properties also play a significant role. There are a number of reported cases,^{13,23} and likely many more unreported instances, in which film mechanical properties change upon sorption of an organic species in a polymer film, with significant impact—a factor of four has been reported²³—upon the magnitude of the response. The mechanical effect of adsorption upon monolayer-based chemically sensitive interfaces has also been used as a means to obtain effective chemical discrimination among classes of organic analytes.²⁴

A thorough and systematic study of the nature and consequences of viscoelastic interactions between acoustic waves and films has been published by Martin and coworkers for both TSM resonators²² and SAW delay lines,¹⁷ including both quantitative theoretical derivations and experimental results. An important conclusion from this work is that attention must be paid to the phenomenon of *resonance* between an acoustic wave and a film of material. This occurs when the acoustic thickness of the film, i.e., the physical thickness corrected for the ratio of acoustic wave velocities in the device substrate and the film material, is an integral multiple of one-quarter of the acoustic wavelength in the film. (A simple analogy is the effect upon light reflection and transmission when an antireflective coating is applied to an optical surface.) When a film is at or near the thickness appropriate for acoustic resonance, major changes in wave velocity and attenuation are likely to confound any attempt to use such a device in the "microbalance mode." This effect is complicated by the fact that both the film modulus and, to a lesser extent, film thickness, are affected by changes in temperature and by the sorption of chemical species into the film.

For a number of reasons, much of our work on the development of acoustic wave-based chemical sensors, in addition to some thin-film characterization studies, has utilized the SAW delay line. As shown schematically in Figure 1, the relatively large, open region between input and output interdigital transducers provides a readily accessible "chemical playground" that is smooth and readily modified by a variety of techniques ranging from physical vapor deposition to monolayer self assembly to chemical derivatization to spin-coating of thin films. Relative to the SAW resonator, the SAW delay line has a more uniform energy distribution, yielding more uniform sensitivity to physical changes over the active region of the surface.²⁵ Under optimal conditions, the SAW resonator offers better signal-to-noise ratios than a comparable delay line—although in many cases signal-to-noise ratios are limited by the temperature coefficient of coating materials,²⁶

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mitigating any advantage. The delay line is more "forgiving" of highly attenuating films than is the SAW resonator, however: major damping of a two-port SAW resonator causes such a device to function effectively as an exceptionally short-path delay line, much inferior, in terms of signal-to-noise ratio, to a purposely-designed delay line.

Martin's paper on viscoelastic perturbations of the SAW delay line delineates an important, film-characteristic-determined regime: that in which the film can be classified as *acoustically thin*.¹⁷ If the film material has non-negligible mechanisms for viscous loss of energy at the device operating frequency, then a film of thickness h with complex shear modulus G is acoustically thin when

$$1.9hf_0v_0\rho \ll |G|, \quad [1]$$

where f_0 is oscillation frequency, v_0 is the unperturbed SAW velocity, ρ is the film density, and 1.9 is a substrate-dependent constant for ST-quartz SAW devices.¹⁷ If, however, the film behavior is highly elastic—in this context, meaning that mechanisms for viscous loss are negligible at the device operating frequency (so that $G' \gg G''$)—then a film with thickness

$$h \ll \Lambda_0 \left(\frac{v_f}{v_0} \right)^2, \quad [2]$$

where Λ_0 is the device acoustic wavelength and v_f is the velocity of acoustic shear waves *in the film*, will behave as acoustically thin. (Eq. 2 was obtained from relationships derived and presented in ref. 16; here, substrate-dependent constants that play a relatively minor role have been omitted.) Thicknesses h less than 1 – 3% of the product $\Lambda_0(v_f/v_0)^2$ are typically considered acoustically thin. Thin films of most metals, ceramics, and some polymers (particularly those in the glassy or crystalline states) can be classified using Eq. 2; when there is any uncertainty, Eq. 1 should be used. Note that h need not be particularly large for a film to be acoustically thick: for a 100-MHz ST-quartz SAW device, a 100-nm-thick film with $|G| = 10^8$ dyn/cm², typical for a polymer film in its rubbery state, is acoustically thick.¹⁷ An acoustically thick film requires a relatively complex treatment of viscoelastic interactions, as detailed in Martin's work.¹⁷

In those happy cases where a film can be considered acoustically thin, perturbations to both SAW velocity, v_0 , and attenuation, α , resulting from changes of mass loading, viscoelasticity, and electrical properties are described by Eqs. 3 and 4:^{17,27,28}

$$\frac{\Delta v}{v_0} = -c_m f_0 \Delta(m/A) + c_{ve} \frac{f_0}{v_0^2} \Delta(hG') - \frac{K^2}{2} \Delta \left(\frac{\sigma_s^2}{\sigma_s^2 + v_0^2 C_s^2} \right) \quad [3]$$

and

$$\frac{\Delta\alpha}{k_0} \approx c_{ve} \frac{f_0}{v_0^2} \Delta(hG'') + \frac{K^2}{2} \Delta\left(\frac{v_0 C_s \sigma_s}{\sigma_s^2 + v_0^2 C_s^2}\right), \quad [4]$$

where $\Delta(m/A)$ is the change in mass/area, $G' + jG'' = G$, $k_0 = 2\pi/\Lambda_0$, film sheet conductivity $\sigma_s = h\sigma$ (σ is bulk conductivity), and the other parameters are defined in Table 1 along with their values for ST-cut quartz. Note that $\Delta v/v_0$ and $\Delta\alpha/k_0$ are the consistently normalized imaginary and real components of the SAW complex propagation factor,^{17,22} hence direct comparison of the magnitudes of changes in these two dimensionless quantities are meaningful.

In this paper, we are concerned primarily with changes in viscoelastic parameters, so the second term on the righthand side of Eq. 3 and the first term on the righthand side of Eq. 4 are of primary interest for analysis of experimentally measured changes in acoustic wave velocity and attenuation.

Crosslinking of a Monolayer Film

Molecularly organized, self-assembled monolayers (SAMs) based upon alkane thiols and their derivatives have found application for everything from model lubricants to chemical sensors.^{29,30} In addition to using them in the role of chemically sensitive interface material,^{24,30,31} our own work combining SAW devices with these versatile films has included real-time, in-situ measurements of the process of self assembly;³² in-situ measurements of monolayer chemical reactions of SAMs;³³ acid/base interactions between SAMs and vapor-phase species;^{34,35} and "mass titrations" of functionalized surfaces with a second chemical species.³⁶ We note that the submonolayer sensitivity of SAW devices to mass and mechanical changes suits them well to the study of SAMs and their interactions.

A potential shortcoming of thiol-based SAMs for practical applications, including chemical sensors, is a lack of long-term thermal stability in oxygen-containing atmospheres: depending upon the particular thiol, the details of substrate preparation, and the like, extended exposure to temperatures above about 100 °C (depending upon alkane chain length) can result in desorption of the SAM and/or oxidation of the thiol headgroup.³⁷⁻⁴¹ In addition, recent solution-phase experiments indicate that, in some solvents, slow desorption or displacement of individual thiols (e.g., by other thiols in solution) may occur.⁴²⁻⁴⁴ A final property of many thiol-based SAMs that can be a liability is a limited degree of "permeability": the hydrocarbon chains of well-ordered thiol-based SAMs formed upon gold single crystals are closely packed, making permeability unlikely, but many applications of SAMs utilize polycrystalline thin films of Au as substrates. In this case, there are defects in the ordering of the SAM at each of the boundaries between the Au grains comprising the thin film. Indeed, our recent work on the Au substrate grain-size dependence of adsorptive phenomena on thiol-based SAMs reveals very significant effects upon the magnitude, repeatability, and reversibility of adsorption from the gas phase.³⁰ Although these defects can potentially be used as an asset to enhance chemical sensitivity³⁰ or selectivity,²⁴ they are "sites of opportunity" for the permeation into the film, potentially leading to film degradation

as well as corrosion of an underlying substrate.

One method to address issues of monolayer long-term thermal stability and permeability is to crosslink the chains of the film. We have reported the synthesis, self assembly, spectroscopic characterization, and (patterned) UV-induced polymerization of the conjugated diacetylenic molecule $\text{HS}(\text{CH}_2)_{10}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_{10}\text{COOH}$, designated DAT, demonstrating its potential for photolithographic masking application.⁴⁵⁻⁴⁹ Successful lithographic pattern definition,⁴⁷ as well as surface Raman spectroscopic data^{46,48} indicate that exposure to ultraviolet (UV) irradiation results in significant crosslinking of this film; Figure 2 depicts the crosslinking process schematically. Additional characterization of the crosslinking process, in terms of its effects on film mechanical properties, is important to better understand the extent to which such a material can be expected to improve upon the long-term stability and reduce the permeability of thiol-anchored films.

Direct, *in-situ* measurement of the film mechanical changes that accompany crosslinking of a single molecular monolayer of DAT provides an additional probe of the nature of the crosslinking process. In this paper, we describe the response of an ST-quartz SAW device to the process of crosslinking a single monolayer of DAT. The results, which agree qualitatively with those obtained recently using a TSM resonator,¹ are consistent with the conversion of a film having the mechanical properties (expressed in "polymer terms") of a relatively elastic, rubbery film to a material with a considerably larger elastic modulus (at least 5×10^{10} dyn/cm²), which is typical, for example, of polymers in the glassy state.

EXPERIMENTAL DETAILS

SAW delay line devices were designed and fabricated at Sandia National Laboratories (SNL) on optical-quality-polished ST-cut quartz substrates with propagation in the *X* direction. Devices have two interdigital transducers, each composed of fifty finger-pairs with $\Lambda_0 = 32$ μm periodicity; v_0 is 3.16 km/s, yielding a center frequency of 97 MHz. Transducers were defined photolithographically from 200 nm-thick Au-on-Cr or Au-on-Ti films; finger length is $50 \Lambda_0$ and center-to-center separation between transducers is $230 \Lambda_0$. Additional details of SAW sensor design can be found elsewhere.²⁶ To support the thiol-anchored monolayers, a 200 nm-thick layer of Au (with a Cr or Ti adhesion layer) was thermally or electron-beam deposited in the wave path using a shadow mask; visual inspection revealed that the Au film retained the optical-quality surface of the underlying substrate.

Each SAW device was configured as the feedback element in an oscillator loop, which included a wide-band amplifier (Hewlett-Packard 8447D), a band-pass filter (K&L Microwave 5BT-95/190-5N), two variable attenuators in series (Hewlett-Packard 8494A and 8495A), a tunable phase shifter (Merrimac PSL-4-100B), 10-dB directional couplers (Anzac DCG-10-4), a frequency counter (Hewlett-Packard 5384A), a vector voltmeter (Hewlett-Packard 8508A) and a computer for data acquisition (Hewlett-Packard 9816). This arrangement yields short-term frequency stability of approximately 0.3 Hz RMS that allows the detection of mass changes as small as 100 pg/cm².⁵⁰ The relationship between the fractional velocity shift caused by changes in the thin film

and the frequency shift measured with a SAW delay-line oscillator circuit is

$$\frac{\Delta f}{f_0} = \kappa \frac{\Delta v}{v_0}, \quad [5]$$

in which κ is the fraction of the center-to-center distance between transducers perturbed (in the present instance, the fraction covered by the Au film and attached monolayer is ~ 0.7). In addition to monitoring the SAW velocity using a frequency counter, the amplitudes of the input and output signals to/from each SAW device were monitored using a vector voltmeter, enabling the insertion loss, L_I (and hence normalized SAW attenuation, α/k_0), to be measured.^{26,50}

$$\frac{\Delta \alpha}{k_0} = \frac{\Delta L_I}{54.6 N_A}, \quad [6]$$

where N_A is the length, in wavelengths, of the region perturbed by the thin film, equal to κ times the IDT center-to-center spacing. For the present experiments, $N_A = 160$.

The synthesis and single-monolayer adsorption of DAT are described in detail elsewhere.^{45,46,48} A DAT-monolayer-modified SAW device was secured in a custom-fabricated stainless-steel test fixture, depicted in Figure 3, including an optical quartz flat window to admit UV irradiation, gas fittings and O-ring seals for purging the SAW device continuously with high-purity nitrogen (to prevent oxidation, a concern particularly if ozone were to form inside the cell during UV irradiation), spring-loaded pin-type electrical contacts for the SAW device, a thermocouple in close proximity to the device, and external electrical connectors. Impedance matching consisted of a single series inductor (470 nH), within the fixture, connected to one comb of each interdigital transducer (IDT); the second comb of each IDT was grounded to the fixture. With this configuration, total insertion loss of about 12 dB is attainable with our Au-IDT, ST-quartz SAW delay lines.

The nitrogen-purged test fixture was maintained in an environmental chamber with temperature control of ± 0.05 °C (in the absence of additional internal heat sources) over many hours. UV irradiation was provided by an unfiltered pen-lamp-type mercury arc source providing 254 nm illumination (Oriel Model 6035), mounted in close proximity to the cell window, approximately 2 cm from the SAW device surface. The angle of incidence of light upon the monolayer-coated device surface was approximately 70° off normal. SAW frequency and attenuation were monitored continually prior to, during, and after UV exposure of the monolayer of DAT. Because the operating UV source warmed the environmental chamber and SAW test fixture significantly (see Results and Discussion), measurement of the net changes resulting from cross linking had to be made by comparing baseline frequency and attenuation prior to activating the UV source with those recorded some hours after the UV source was switched off and the thermocouple and unchanging oscillation frequency both indicated that the SAW device had returned to its pre-exposure temperature. As detailed in the next section, appropriate control experiments were conducted to verify that the measured shifts were indeed associated with monolayer crosslinking.

RESULTS AND DISCUSSION

Figure 4 shows the SAW frequency as a function of time before, during, and after the photocrosslinking of a monolayer of $\text{HS}(\text{CH}_2)_{10}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_{10}\text{COOH}$ (DAT) chemisorbed on an Au film on the device surface. During the 24-hour UV exposure tracked by the data of Figure 4, a temperature increase was indicated by the thermocouple incorporated in the SAW test fixture as a result of the continuous illumination. Once UV illumination was discontinued and temperature returned to within 0.06°C of its initial value, a net frequency change of $+11 \pm 1$ ppm, corresponding to a fractional velocity shift of $+16$ ppm ($\kappa = 0.7$; see Eq. 5), was measured as a result of the film crosslinking process.

Figure 5 shows the SAW attenuation change normalized to wavenumber ($\Delta\alpha/k_0$), as well as temperature inside the test fixture, during the same experiment represented by Figure 4. Because the low-mass thermocouple tip was immersed in flowing N_2 , it may have experienced a smaller temperature excursion than the SAW device, which was contacted by the same flowing N_2 but also in intimate thermal contact with the test fixture (which, in turn, was heated by the UV arc lamp). The attenuation data show a net change in α/k_0 of -4 ± 2 ppm and the net temperature change is approximately -0.06°C .

To validate the results of this crosslinking experiment, one replicate and several control experiments were performed. In fact, the data of Figures 4 and 5 were obtained from the second such UV crosslinking experiment. In the first experiment, the sample was illuminated for several periods of 1 - 3 hours, using the same geometry as for the data of Figure 4, and showed only a few ppm of net positive frequency shift each time. When the total time of exposure reached ca. 11 h, no further net change was noted upon further UV exposure. The overall net frequency shift from this series of exposures was 11 ± 3 ppm, the greater uncertainty a result of adding together several separate, smaller changes. Thus, the exposure time of 24 h used for the data of Figure 4 was chosen to insure that crosslinking was complete.

To ascertain what role, if any, was played by thermally and UV-stimulated desorption (of water or other surface contaminants) in the data obtained from the two samples described above, a third sample was prepared and UV crosslinked prior to placing it into the SAW test fixture and UV-irradiating the coated SAW device. This sample was otherwise handled identically to the two uncrosslinked samples. (For all three samples, there was a gap of some days between film preparation and UV irradiation in the SAW fixture, during which time the coated SAW devices were stored in the dark in a dry atmosphere). UV irradiation of the pre-crosslinked film yielded a net frequency shift of < 2 ppm for an irradiation time of 5 h, confirming that UV crosslinking is the main source of the frequency shift recorded for the two initially uncrosslinked samples, and that impurity desorption does not play a significant role.

The sensitivity of film-coated SAW devices to small temperature changes is well established.²⁶ The UV irradiation process produced a significant temperature increase in the SAW fixture during illumination, although temperature did return to within 0.06°C of its initial value prior to measuring the net frequency shift. Nevertheless, the temperature dependence of two of the SAW

devices bearing crosslinked films of DAT was examined. By intentionally raising the temperature of the entire environmental chamber (as opposed to the localized heating created by the mercury arc lamp) over the course of several hours, then bringing the temperature to its original value, we probed two issues. First, the temperature coefficient of a crosslinked DAT-coated SAW device was determined to be -11.9 ± 0.4 ppm/ $^{\circ}\text{C}$. To obtain the +11 ppm frequency shift recorded in Figure 4, therefore, would require the temperature to be cooler by 0.9 $^{\circ}\text{C}$ after crosslinking than before (about 15 times greater than the before/after temperature difference actually measured, see Figure 5). Second, the temperature cycle demonstrated how accurately the temperature can be "reset" to its initial value, and how close the final SAW frequency can be to its initial value, after a several-hour temperature excursion, if no crosslinking or other physical change occurs during this time. The temperature returned to within 0.03 $^{\circ}\text{C}$ of its initial value for both temperature ramp experiments, and the SAW frequency returned to within 0.6 ppm of its initial value in both cases, verifying that the temperature control and frequency stability of our system are adequate.

The DAT molecule is particularly convenient for this SAW-based crosslinking study because the polymerization reaction (Figure 2) does not involve any mass change; SAW frequency changes should therefore be wholly attributable to mechanical effects. Another consideration is that the conjugated double and triple bonds shown in Figure 2 should impart finite electrical conductivity to the crosslinked monolayer, and SAW devices can respond to changes in film electrical properties (see Eqs. 3 and 4). However, acoustoelectric effects are operative over only a relatively narrow "window" of sheet conductivity,¹⁴ and our previous measurements have shown that a minimum of 1 nm of Ni, for example, is required for a measurable acoustoelectric perturbation of the SAW on ST-quartz.⁵⁰ We believe the conductivity of this organic material is less than one-half that of metallic nickel and therefore too small to perturb the SAW *via* acoustoelectric interactions. Furthermore, acoustoelectric effects on SAW velocity are accompanied by significant attenuation changes: a thin film passing through the conductivity of maximum acoustoelectric coupling produces a change in normalized SAW attenuation that is equal in magnitude and opposite in sign to the fractional change in SAW velocity.⁵⁰

Having established that most or all of the +16 ppm velocity shift is a consequence of modulus increase due to crosslink formation allows calculation of the change in DAT monolayer shear modulus. First, it should be determined if this film can be treated as acoustically thin, as described in the Introduction. With a thickness of 2.4 nm and density of 1.3 g/cm³, the DAT film has a value of 1.7×10^7 dyn/cm² for the product on the lefthand side of Eq. 1, which is the general condition to be satisfied if a film is acoustically thin. Although the magnitude of the complex shear modulus of the uncrosslinked DAT film is unknown, it is in all probability greater than 10^8 dyn/cm², a typical value for $|G|$ of rubbery polymers.^{4,17} We believe this to be the case for three reasons: (1) rubbery polymers lack the ordering imposed upon a DAT monolayer by adsorption of head groups upon the Au substrate, which enhances the number of $\text{CH}_2 - \text{CH}_2$ van der Waals interactions within the DAT layer; (2) rubbery polymers lack the chemisorption-based, head-group-to-surface attachment points that organize the DAT layer, making it more rigid; (3) "typical" rubbery polymers do not have carboxylic acid groups disposed in close proximity to one another, as in the case for the tail groups of adjacent DAT molecules, providing an opportunity for intermolecular hydrogen bonding and further stiffening the DAT film.

Granting the arguments that the uncrosslinked DAT monolayer can be treated as acoustically thin, the recorded velocity shift of +16 ppm corresponds to a *change* in G' of 5×10^{10} dyn/cm² (from the second term of Eq. 3) upon UV crosslinking. This can be considered as a lower bound for the shear storage modulus, G' , of the fully crosslinked film. Interestingly, a recently completed set of measurements by Shinn *et al.*^{1,51} using quartz thickness-shear mode (TSM) resonators yielded consistent and complementary results. From in-situ measurements made during the UV crosslinking of films of the same DAT monolayer under very similar conditions, they concluded that the shear modulus of the fully crosslinked film is between 100 and 1000 times that of the initially uncrosslinked film. Combining their results with those presented in this paper leads to the conclusion that G' for the uncrosslinked film is between 5×10^7 and 5×10^8 dyn/cm², and G' for the fully crosslinked film is 5×10^{10} dyn/cm². Note that this is consistent with the hypothesis made above, that G' for the uncrosslinked polymer exceeds 1.7×10^7 dyn/cm², though apparently not by a wide margin.

Although the change in SAW attenuation accompanying monolayer crosslinking is only about one-fourth that of the velocity shift, we do believe the measured effect is real. The observed decrease in normalized attenuation of about -4 ppm is consistent with a modest amount of additional restriction of the relative motion of each diacetylenic thiol relative to its neighbors as a consequence of crosslink formation. Relative chain-chain "rubbing" is one means by which aliphatic chains can dissipate acoustic energy imparted by the acoustic wave; the phenomenon of increased shear modulus accompanied by decreased viscous loss as a consequence of polymer crosslinking is general.⁵² Indeed, increases in acoustic wave velocity with concomitant decreases in attenuation have been previously reported in the study of photocrosslinking of polymer-based photoresists.^{2,3}

CONCLUSIONS

Measuring the modulus, and changes therein, in a single molecular monolayer is not a simple task. The results in this paper and those in a soon-to-be-published study⁵¹ of the same material using the TSM resonator (also known as the quartz crystal microbalance) suggest that SAW and TSM devices can be used in a complementary fashion to obtain both changes in, and absolute values of, monolayer shear modulus before and after crosslinking. In the present study, those values for a diacetylenic thiol-based monolayer are about 10^8 and 5×10^{10} dyn/cm² for the uncrosslinked and fully photocrosslinked films, respectively.

We point out that the precondition of acoustic "thinness" required to interpret SAW responses unequivocally as either pure mass loading or purely elastic modulus changes is not easily met. For the present monolayer film, which is a mere 2.3 nm thick, the product $hf_0v_0\rho$ is about 10^7 dyn/cm², and this value must be less than the shear modulus of the material if the film is to be considered acoustically thin. Our results, coupled with some knowledge of the nature of the bonding and interactions within the monolayer, did in fact lead us to conclude that the DAT monolayer is acoustically thin, and comparison of SAW and TSM results support this conclusion. However, it is also clear that rubbery polymer films commonly used for chemical sensor

applications, typically cast in films 50 – 1000 times thicker than the DAT monolayer examined here, are very often *not* acoustically thin.

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Table 1. Material Constants for X-Propagating, ST-Cut Quartz SAW Substrates

Description and symbol	Magnitude and units
Coefficient of mass sensitivity, c_m	1.29 cm ² g ⁻¹ MHz ⁻¹
Coefficient of viscoelastic sensitivity, c_{ve}	1.55 cm ² g ⁻¹ MHz ⁻¹
SAW velocity, v_0	3.16 km s ⁻¹
Electromechanical coupling coefficient, ^a K^2	0.11%
Capacitance/length, ^b C_s	0.5 pF cm ⁻¹

^aA measure of the piezoelectric strength of the substrate

^b $C_s = \epsilon_s + \epsilon_0$, the respective permittivities of the substrate and free space

FIGURE CAPTIONS

Figure 1. Surface acoustic wave-based delay-line oscillator, showing the interaction region between the SAW and a thin surface-immobilized film. For the crosslinking of diacetylenic monolayers, the film is self assembled on a 200-nm-thick film of Au.

Figure 2. Schematic depiction of a monolayer of the conjugated diacetylenic thiol $\text{HS}(\text{CH}_2)_{10}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_{10}\text{COOH}$ before and after photocrosslinking. This crosslinking process does not result in a change of mass, since no chemical species are lost in the process of forming the new bonds.

Figure 3. Drawing of the SAW test fixture used for in-situ measurement of the polymerization of diacetylenic thiol monolayers. The top half of the fixture contains gas inlet and outlet, a "well" to locate the SAW device, surrounded by an O-ring to provide a gas-tight seal; the two large holes within the O-ring are the gas inlet and outlet, and the four smaller holes at the fixture corners are for securing the two parts of the fixture together. The bottom half of the fixture contains spring-loaded pin contacts for the SAW transducers, electrical connectors, and an optical port (quartz window not shown) to provide illumination of the SAW device surface. A cutaway of the bottom of the fixture (which can also be used for in-situ ellipsometric measurements, hence the reason for two optical ports) is shown at the right. Note that the SAW device (shown suspended between the two fixture pieces) is oriented with transducers and monolayer-coated Au pad facing down, to make electrical contact and to expose the film to the UV light.

Figure 4. SAW frequency shift (1 ppm = 97 Hz) as a function of time before, during, and after exposure of the diacetylenic thiol monolayer-coated device to 254-nm illumination from a mercury arc lamp. The net frequency shift is approximately +11 ppm.

Figure 5. Normalized SAW attenuation change, $\Delta\alpha/k_0$, (left axis) and temperature inside the fixture (right axis) as a function of time before, during, and after crosslinking of the same diacetylenic thiol monolayer characterized in Figure 4. The net attenuation change is about -4 ppm and the net temperature change about -0.06 °C.

Figure 1, Ricco et al

Figure 3, Ricco et al.

Figure 4, Ricco et al.

Figure 5, Ricco et al.