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A number of gas and vapor sensors have been constructed using surface acoustic waves (SAW) to detect the presence of adsorbed molecules [1-4]. Since the acoustic energy of the SAW is confined to the near-surface region of the substrate, the propagation characteristics are extremely sensitive to surface perturbations. Several mechanisms have been identified whereby adsorbed species may perturb the SAW propagation characteristics. Changes in surface conductivity [5], stiffness [6], dielectric constant, or mass density [6], alter the SAW velocity and/or attenuation and may contribute to a SAW sensor response. The surface wave propagation path is typically covered with a coating which selectively sorbs the species to be sensed. By judicious choice of coatings, selective sensors may be constructed.

We depart from the conventional implementation of SAW devices as gas sensors to describe how they may be used to measure adsorption isotherms and to perform thermal desorption spectroscopy. Adsorption isotherms are measurements, made at constant temperature, of surface coverage as a function of gas or vapor partial pressure for the species of interest. In thermal desorption spectroscopy (TDS) a measurement is made (at constant pressure) of surface coverage while ramping the surface temperature. TDS measurements are typically performed with single crystals under ultra-high vacuum conditions to study fundamental aspects of adsorption. By using the SAW device to measure surface coverage, isothermal measurement and thermal desorption spectroscopy may be performed with a single solid state device rather than the conventional mass spectrometer, albeit without the mass specificity offered by such an instrument. The device may thus be used in atmospheric sensor applications as well as in UHV studies.

The surface acoustic wave thermal desorption sensor utilizes a piezoelectric single crystalline ST-quartz substrate with input and output interdigital transducers positioned on either side of a meander-line heater, Fig. 1. The 20 finger-pair transducers have a periodicity of 32 μm , giving rise to a center frequency of 97 MHz. The acoustic beamwidth of the device is approximately 3 mm. The meander-line heater has a conductor width equal to 4 acoustic wavelengths; since this width is a multiple of half the acoustic wavelength, wave reflections by the heater are minimized.

In order to gain maximum sensitivity in measuring surface coverage, the device is used as the feedback element of an oscillator circuit. Adsorbed molecules perturb the SAW propagation velocity and hence the oscillator frequency due to mass loading of the wave. The SAW device functions as an extremely sensitive microbalance, capable of measuring submonolayer coverage of the quartz surface. Short term changes in surface mass density on the order of 10^{-10} g/cm² are readily measurable.

Figure 1 Surface acoustic wave device configuration used for measuring adsorption isotherms and thermal desorption spectra of organic vapors.

Adsorption Isotherms

In order to examine the coverage dependence upon vapor pressure, or adsorption isotherm, the SAW sensor was used to measure coverage while continuously varying ambient vapor concentration. A vapor/N₂ mixture was introduced into the sealed device chamber, continuously varying the vapor pressure from 3% to 97% of the saturation vapor pressure (p_s) at 20 C.

As seen in the adsorption isotherm of Fig. 2, the frequency shift occurring during methylene chloride (CH₂Cl₂) exposure indicates a general increase in coverage with increased vapor fraction p/p_s . The solid line in Fig. 2 shows the variation in vapor coverage with increasing p/p_s , while the dashed line is for decreasing p/p_s . Considering that monolayer coverage corresponds to a surface density of roughly 10^{15} cm⁻², full monolayer coverage by methylene chloride should result in a frequency shift of 21 ppm [7]. The horizontal line shows the frequency shift calculated for full monolayer coverage. The entire adsorption/desorption cycle was performed over a two hour period. The device shows little hysteresis and it is apparent that surface coverage goes to zero when the organic vapor is eliminated from the chamber. Coverage increases nearly monotonically with vapor pressure, reaching a full monolayer for p/p_s near .85. For greater values of p/p_s , a rapid increase in coverage is observed, probably due to multilayer formation (condensation) [7].

Thermal Desorption Spectra

Thermal desorption measurements can be made with the device shown in Fig. 1 by ramping the surface temperature while simultaneously monitoring the oscillation frequency. The SAW device functions as an indicator of surface coverage, substituting for a mass spectrometer in conventional thermal desorption spectroscopy. In order to demonstrate the measurement of thermal desorption using a SAW device, the vapor mixture was maintained at 10 C while the substrate surface temperature was ramped from 10 to 50 C. A static vapor/ N_2 mixture was maintained in the device chamber stabilizing at $p/p_s = 0.8$, resulting in an initial coverage of slightly less than a monolayer.

Figure 2 Adsorption isotherm revealing surface coverage for various partial pressures of methylene chloride. The horizontal line indicates monolayer coverage.

To increase the surface temperature monotonically, the current through the meander-line heater was ramped from 0 to 75 mA over a period of 375 seconds. During the ramp cycle, the resistance of the meander-line heater was monitored, as well as the SAW oscillator frequency. Resistance of the Cr/Au heater serves as an excellent measure of the surface temperature of the device. (To accurately obtain the surface coverage as a function of surface temperature, it is necessary to subtract the oscillation frequency measured in vapor from that obtained in nitrogen only.)

The TDS curve of Fig. 3 shows that surface coverage decreases dramatically as the surface temperature is increased. In the TDS of methylene chloride, the overall frequency shift is 19 ppm, agreeing closely with the expected shift of 21 ppm for removal of a full monolayer. The features appearing in the adsorption isotherm (Fig. 2) are duplicated in the TDS of Fig. 3, with the interchange of temperature and pressure as the coverage determining variable.

Figure 3 SAW thermal desorption spectrum obtained in a methylene chloride ambient with $p/p_s = .8$ at 10 C.

It has been shown that by incorporating a heater as an integral part of a SAW device, a sensor can be constructed which is capable of measuring thermal desorption spectra. A greater spread in the temperatures at which molecules are desorbed, and thus greater discrimination between species, could be obtained by using coatings which form stronger chemical bonds rather than relying on physisorption.

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References

1. H. Wohltjen and R. Dessy, Anal. Chem., 51, 1458, 1465, 1470, 1979.
2. A. Bryant, D. L. Lee, and J. F. Vetelino, 1981 Ultrasonics Symposium Proceedings, IEEE: New York, p. 171, 1981.
3. A. W. Barendsz, J. C. Vis, M. S. Nieuwenhuizen, E. Nieuwkoop, M. J. Vellekoop, W. J. Chijssen, and A. Venema, 1985 Ultrasonics Symposium Proceedings, IEEE: New York, 1985.
4. A. D'Amico, A. Palma, and E. Verona, 1982 Ultrasonics Symposium Proceedings, IEEE: New York, p. 308, 1982.
5. A. J. Ricco, S. J. Martin, and T. E. Zipperian, "Surface Acoustic Wave Gas Sensor Based on Film Conductivity Changes", Sensors and Actuators, in press.
6. H. Wohltjen, Sensors and Actuators, 5, 307 1984.
7. S. J. Martin, A. J. Ricco, D. S. Ginley, and T. E. Zipperian, "Isothermal Measurement and Thermal Desorption Using SAW Devices", submitted to IEEE Transactions on UFFC, special issue on acoustic sensors, 1986.