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Abstract

In the course of developing a sensor for simultaneous humidity and temperature sensing, we have investigated surface-acoustic-wave (SAW) transducers for use as tools in characterizing materials of interest in sensing applications. In this paper we report a computer-controlled test system for characterizing oscillator-based sensors and demonstrate the utility of SAW oscillator measurements for gaining insight into sorption processes in glassy polymers.

Introduction

Surface-acoustic-wave (SAW) devices are now being used extensively in the storage and processing of analog and digital signals. Their applications range from sophisticated radar, sonar and communications systems to mass-produced components for radio and television receivers. Since surface wave propagation is very sensitive to external variables, low-temperature-coefficient cuts and design are employed, and protective packaging - typically hermetically sealed - is used for signal processing applications requiring immunity from environmental effects.

From the viewpoint of the sensor technologist, in contrast, strong sensitivity to a particular environmental effect is at the heart of development of a useful sensor for that effect. Thus, in recent years, considerable interest has been evinced in developing physical and chemical sensors based on SAW technology. A preliminary report of a pressure sensor appeared in 1975 [1]. The first chemical sensor based on SAW technology was a vapor sensor reported in 1979 [2], and since then numerous SAW sensors of chemical and biological interest have been discussed [3-8].

We are particularly interested in the development of vapor sensors for water vapor, and have demonstrated simultaneous humidity and temperature sensing with a dual-delay-line SAW device [9,10]. When used in a dual-oscillator configuration [10], this sensor produces direct frequency outputs that are easily measured with a digital frequency counter. One frequency is linearly related to temperature, while the other is a function of relative humidity.

Historically, a variety of techniques has been brought to bear on the complex problem of water vapor interaction with solids [11]. Water-polymer interactions have been extensively studied with a wide range of physical, analytical and spectroscopic techniques [12]. Gravimetric measurements have been used in the study of both energetics and kinetics of sorption [13]. Most recently, Huang [14] attempted to apply thermodynamic analysis to electrical data from polymeric humidity sensors, in an effort to gain an understanding of the energetics of sorption from direct sensor measurements at several temperatures. Since propagation of surface acoustic waves is highly sensitive to changes in mass and mechanical properties of overlayers deposited in the propagation region of SAW devices [7], it should be possible to use the device as a transducer to aid in characterizing materials of interest in sensing applications as they interact with vapors. This paper de-

monstrates the use of SAW sensors for studying the water-vapor sorption energetics and kinetics in hygroscopic polymers.

Experimental

SAW device fabrication:

The experimental device used 15-finger-pair interdigital transducers (IDT's) of Al having a periodicity of 52.5 μm , center-to-center spacing between transducers of 5 mm and an aperture of 3.5 mm. Conventional photolithography was used to define the pattern. Multiple delay lines were fabricated on a 0.5 mm thick, 128°-rotated Y-cut, X-propagating LiNbO_3 substrate. The uncoated delay line had a center frequency of 74.3 MHz, time delay of 1.3 μsec , and a 6-dB bandwidth of approximately 4.8 MHz. The untuned, unmatched insertion loss in a 50-ohm system was 10 dB.

Polymer materials and coating:

Hygroscopic polymers were deposited by spin-coating from solution onto the delay lines, followed by thermal treatment. All were in the glassy state at temperatures used for this investigation. Polyimide (PI) films of 2-4 μm thickness were deposited by using PI2545 solution (DuPont) and baking for one hour at 130°C in air. The film was then patterned using conventional photolithography. In this state the film is partially imidized and contains some residual hygroscopic solvent. Fully imidized, solvent-free and high density polyimide was prepared on some sensors by baking for two hours at 350°C in N_2 . Both partially and fully imidized films were tested. Cellulose acetate butyrate (CAB) films of 1-5 μm thickness were deposited from diacetone alcohol solution. Polymers of 17, 39 and 51 wt.% butyrate, respectively, (Eastman Chemicals Co.) were used. These films were baked for one hour at 130°C under vacuum. Cross-linked CAB films of 1-5 μm thickness were also prepared by similar means, using a proprietary solution composition.

Sensor configuration:

For most experiments the SAW delay line was connected in the oscillator configuration [10]. The amplifier was a model HP8447A broad-band amplifier (Hewlett-Packard), driving a 50-ohm variable attenuator (HP335C), with the delay line in the feedback path of the amplifier to produce a delay-line-stabilized oscillator. The oscillation frequency was measured with a digital frequency counter (HP5385A) for display and transfer via GPIB. Since multiple delay lines were fabricated on a single substrate, some sensors were configured as dual oscillators by connecting adjacent delay lines to form separate oscillator loops.

Test cell:

The SAW sensor was mounted inside an air-tight stainless steel cell provided with gas inlet and outlet, rigid insulated signal feedthroughs and a thermocouple. For most experiments the thermocouple was attached to the LiNbO_3 crystal.

Test system configuration:

The test cell was inserted into a computer-controlled sensor test system capable of controlling cell temperature and pressure, test-gas dew point, and flow rate. For this investigation, cell temperature and gas dew point were controlled in order to produce a well-defined relative humidity (RH) inside the test cell. Humidity could be varied from near 0% RH to 100% RH by controlling the mixing ratio of dry and wet nitrogen gas within a moisture calibrator (Ondyne Model 10). Cell temperature could be varied between -40° and $+100^{\circ}\text{C}$ by controlling a programming potentiometer remote to an oven (Delta MK2300). Step functions of relative humidity within the test cell were generated by controlling two solenoid valves to isolate the cell from the gas stream.

All test system measurement and control functions were implemented with a general-purpose interface (Elexor Associates PL-100) under the control of a Tandy/Radio Shack Model 100 computer. Frequency measurements from the SAW oscillators were ported to the computer from the digital counter via an IEEE488 \leftrightarrow RS-232C protocol converter (Network Supply GPNET Model 10). Custom software written for the system was used to generate humidity and temperature parameters within the test cell, and collect isotherms, isobars and transient-response data. All system parameters and sensor test data were stored temporarily in the computer, then transferred as necessary via modem to a mainframe (VAX 11/785).

Results

Dual-delay-line sensor:

A sensor having two identical SAW delay lines was patterned with PI2545 such that one delay line was coated with partially imidized polyimide, while the other was uncoated. As expected, frequency of the 'coated' oscillator decreases with increasing relative humidity, at constant temperature. This is shown in Fig. 1.

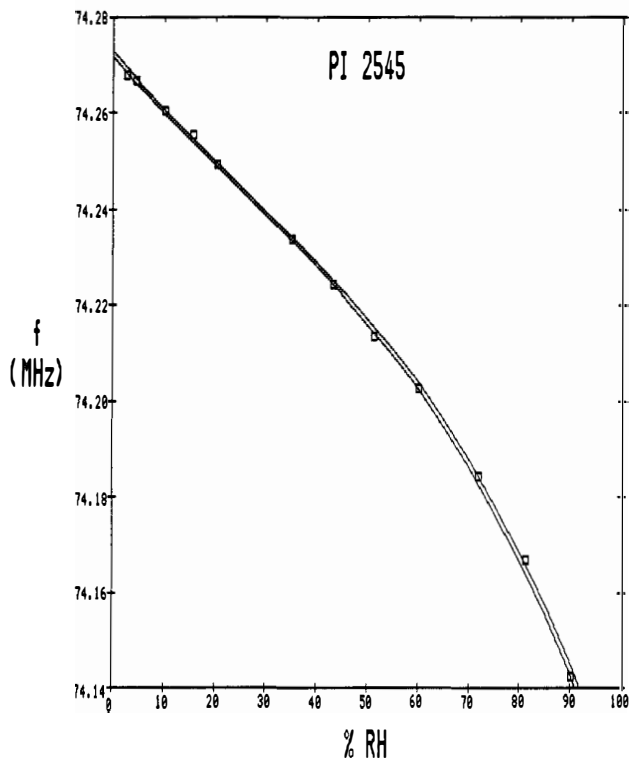


Fig. 1. Variation of SAW oscillator frequency with relative humidity for a polyimide-coated delay line at 23.5°C .

Between 5% and 60% RH, the frequency varies almost linearly with humidity, with a slope of $-1.1\text{ KHz per }1\%$ change in RH. It is also apparent that the 'coated' oscillator operates satisfactorily for relative humidity values approaching 100%.

Fig. 2 presents the combined effects of humidity and temperature on the two oscillators. Both were connected in the oscillator configuration and oscillator frequencies were recorded from both as a function of humidity, at a series of temperatures between 10° and 40°C .

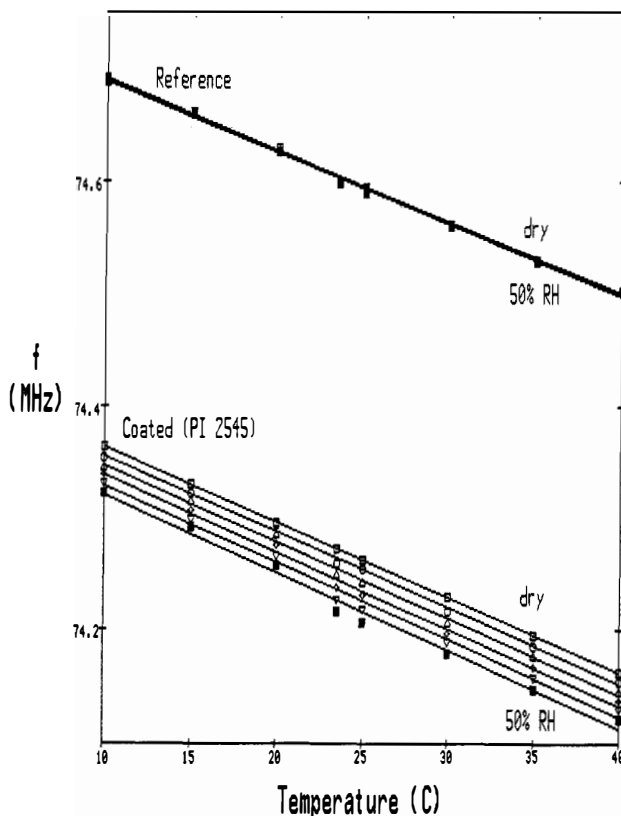


Fig. 2. Variation of oscillator frequency with temperature and humidity for uncoated and polyimide-coated delay lines.

Frequencies at equally spaced RH increments (dry gas, 10%, 20%, 30%, 40%, 50% RH) are plotted at each temperature for each oscillator. The lines drawn through the data points in Fig. 2 are least-squares fits. Both oscillators show similar, but not identical, temperature effects. The TCF of the polymer-coated delay line is slightly larger in magnitude than that of the reference. In addition, the reference oscillator is only weakly perturbed by humidity variations until relatively high humidities (RH $>$ 75%) are reached, whereas the coated oscillator is strongly sensitized to humidity within the temperature range studied.

Differential thermodynamic functions:

The differential enthalpy, entropy, and free energy of sorption of water in each polymer were calculated from the temperature variation of frequency in the sorption isotherms, using the conceptual approach of Huang [14]. A linear background correction for the TCF of the polymer-coated sensor in dry gas was made. The experimental thermodynamic functions for water in the cellulose derivative CAB 381 are presented in Fig. 3, calculated from adsorption isotherms at 10.1, 19.8, 29.9, 40.0 and 49.9°C .

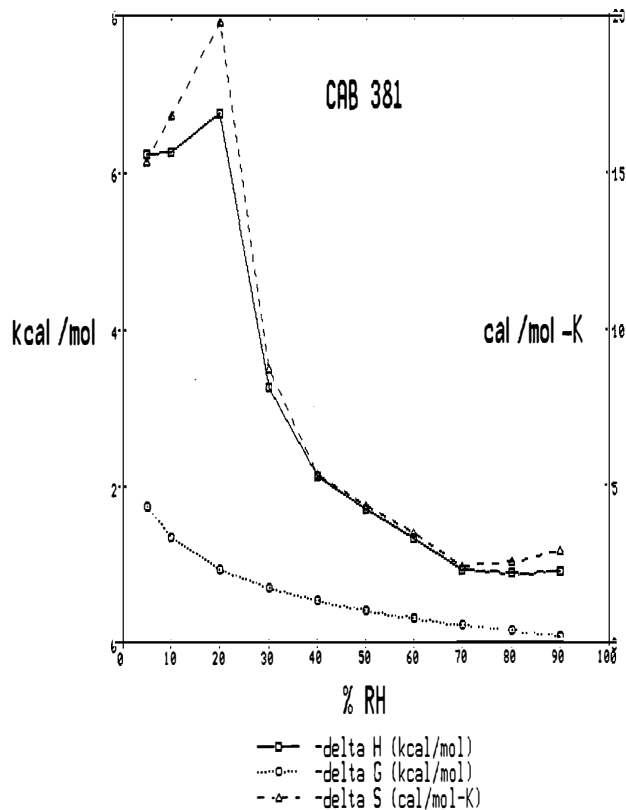


Fig. 3. Differential thermodynamic quantities for water in CAB 381 polymer as a function of relative humidity. Left ordinate: $-\Delta\bar{H}$, $-\Delta\bar{G}$. Right ordinate: $-\Delta\bar{S}$.

A physical adsorption of the water vapor is indicated by the range of differential enthalpies observed. The large negative and relatively constant $\Delta\bar{H}$ at low relative humidities suggests strong bonding with the polymer, possibly involving two hydrogen bonds per water molecule. The increasingly negative $\Delta\bar{S}$ found at low humidities also suggests a decrease in randomness of the adsorbed water molecules. Taken together, the approximately constant $\Delta\bar{H}$ and increasingly negative $\Delta\bar{S}$ suggest Langmuir-type adsorption behavior within the first monolayer [15], i.e., up to about 20% RH in Fig. 3.

Following completion of the monolayer, the rapid decline in magnitude of the differential enthalpy with increasing humidity suggests that multilayer adsorption is occurring, wherein cohesive interactions between molecules of the outer layer(s) are much more important (i.e., contribute to the thermodynamic equilibrium) than are interactions of the first layer [16]. The similarity in shape of the enthalpy and entropy functions (in this regime of relative humidity) suggests that the sorbed water which does contribute to thermodynamic equilibrium is approaching the liquid state [17].

Sorption Kinetics:

The transient response of SAW oscillator sensors to step changes in humidity was studied by monitoring the frequency at constant temperature. Very rapid response was generally observed from the CAB-coated sensors. The time constant, τ , for both adsorption and desorption was 5 ± 1 s at room temperature, in agreement with the amplitude and phase time dependence [10]. Much slower response was observed from partially and fully imidized PI coatings, with a time dependence that varied with step direction and humidity at initiation of

the step. A typical transient-response result from a fully imidized PI coating (two sequential steps in humidity) is shown in Fig. 4.

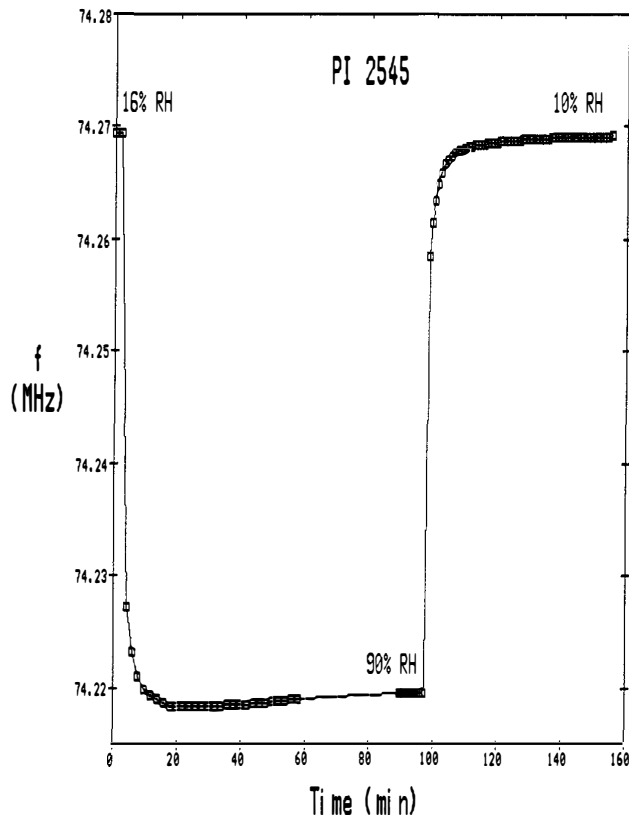


Fig. 4. Transient response of polyimide-coated SAW delay line at 23.5°C.

Analysis shows that the evolution of frequency with time in Fig. 4 does not follow a single exponential, although diagnostic plots (log frequency vs. log time) [18] of the adsorption and desorption data do reveal regions of characteristic slope. Three regimes or stages in the kinetics may usually be discerned in each step: an initial, rapid stage is followed by a slower intermediate stage, followed by a slow transition to thermostatic equilibrium. We propose that the regimes correspond to 1) rapid adsorption/desorption at surface sites; 2) diffusion of water in the polymer; and 3) relaxation of the plasticized polymer, respectively. There is, of course, overlap in the kinetics so that rapid site adsorption/desorption is envisaged as being concurrent with the other, slower, processes.

The 'undershoot' evident in the frequency during the adsorption step of Fig. 4 is frequently, but not always, observed, and only in the adsorption process. Analogous transients have been noted by others [5] during the adsorption of hydrogen on Pt. A possible explanation is found in the perturbation result of Wohltjen (eqn. 1 of ref. 7), in which the predicted frequency shift due to the presence of an overlayer in the SAW propagation region contains a term dependent on the overlayer mass per unit area and a term of opposite sign containing overlayer modulus. During adsorption of water, it is logical that modulus changes near the crystal/polymer interface should occur subsequent to mass changes in the polymer film. The effect of mass increase should be reflected almost instantaneously as a decrease in frequency, whereas any decrease in polymer modulus should lag somewhat and result in a small increase in frequency, as is seen in the adsorption step in Fig. 4.

In the case of several of the polymers studied, the desorption kinetics are found to differ from adsorption kinetics by having a higher initial rate and a more extended diffusion-controlled regime. The higher initial rate probably reflects a slightly lower energy barrier for desorption of surface water. The more lengthy diffusion-control regime in desorption is likely due to the necessity for all water to diffuse out of the bulk of the polymer before it can be released at the surface.

Conclusions

Measurements of SAW sensor frequencies in an automated test system have been used in a study of the thermodynamics and kinetics of water-vapor sorption in some hygroscopic polymers. The thermodynamic results indicate physical adsorption, point to a Langmuir-type behavior in the monolayer and suggest that a liquid-like multilayer description is appropriate at higher humidities. The kinetic results are consistent with a multistage sorption process that is expected for glassy polymers. We believe that these results demonstrate the usefulness of the SAW transducer as a new tool for materials research. It is possible to utilize its high surface sensitivity as a complement to traditional thermal and gravimetric methods.

References

- [1] T. M. Reeder and A. J. Demaria, U. S. Patent 3,978,731, Sept. 1976.
- [2] H. Wohltjen and R. E. Dessy, "Surface acoustic wave probe for chemical analysis," Anal. Chem., vol. 51, pp. 1458-1475, 1979.
- [3] A. Bryant, D. L. Lee and J. F. Vetelino, "A surface acoustic wave gas detector," Proceedings IEEE 1981 Ultrasonics Symp., pp. 159-162.
- [4] C. T. Chuang, R. M. White and J. J. Bernstein, "A thin-membrane surface-acoustic-wave vapor-sensing device," IEEE Electron Device Lett., vol. EDL-3, No. 6, pp. 145-148, 1982.
- [5] A. D'Amico, A. Palma and E. Verona, "Surface acoustic wave hydrogen sensor," Sensors and Actuators, vol. 3, pp. 31-39, 1983.
- [6] J. E. Roederer and G. J. Bastiaans, "Microgravimetric immunoassay with piezoelectric crystals," Anal. Chem., vol. 55, pp. 2333-2336, 1983.
- [7] A. Snow and H. Wohltjen, "Poly(ethylene maleate)-cyclopentadiene: A model reactive polymer-vapor system for evaluation of a SAW microsensor," Anal. Chem., vol. 56, pp. 1411-1416, 1984.
- [8] H. Wohltjen, A. Snow and D. Ballantine, "The selective detection of vapors using surface acoustic wave devices," Proceedings 1985 Int. Symp. on Solid-State Sensors and Actuators, pp. 66-70.
- [9] J. G. Brace and S. G. Joshi, "Investigation of a surface-acoustic-wave sensor for simultaneous detection of relative humidity and temperature," Proceedings 1985 Int. Symp. on Moisture and Humidity, pp. 225-227.
- [10] S. G. Joshi and J. G. Brace, "Measurement of humidity using surface acoustic waves," paper no. PB-10 presented at the IEEE 1985 Ultrasonics Symp., San Francisco, CA., Oct. 16-18, 1985.
- [11] J. Texter, K. Klier and A. C. Zettlemoyer, "Water at surfaces," in Prog. Surf. and Membrane Sci., vol. 12. New York: Academic Press, 1978, pp. 327-403.
- [12] Ibid., pp. 330-331.
- [13] J. A. Rupley, P.-H. Yang and G. Tollin, "Thermodynamic and related studies of water interacting with proteins," in Water in Polymers, ACS Symp. Ser.; 127. Washington: American Chemical Society, 1980, pp. 111-132.
- [14] P. H. Huang, "Electrical and thermodynamic characterization of water vapour/polymeric film system for humidity sensing," Sensors and Actuators, vol. 8, pp. 23-28, 1985.
- [15] A. W. Adamson, Physical Chemistry of Surfaces, third ed. New York: Wiley, 1976, pp. 548-634.
- [16] H.-G. Burghoff and W. Pusch, "A model of physical adsorption of gases," J. Appl. Polymer Sci., vol. 24, pp. 1479-1495, 1979.
- [17] Adamson, p. 602.
- [18] C. H. M. Jacques, H. B. Hopfenberg and V. Stannett, Polym. Sci. & Tech., vol. 6, p. 73, 1974.