Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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V. P. Gilbert[a]; P. R. Bienkowski[a]; H. D. Cochran[b]
[a] Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee [b] Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

To cite this Article Gilbert, V. P. , Bienkowski, P. R. and Cochran, H. D.(1988) 'Proposed Technique for Surface Dynamics Measurements at High Pressure', Separation Science and Technology, 23: 12, 1941 — 1948
To link to this Article: DOI: 10.1080/01496398808075674
URL: http://dx.doi.org/10.1080/01496398808075674

SEPARATION SCIENCE AND TECHNOLOGY, 23(12&13), pp. 1941-1948, 1988

PROPOSED TECHNIQUE FOR SURFACE DYNAMICS MEASUREMENTS AT HIGH PRESSURE

V. P. Gilbert and P. R. Bienkowski
Department of Chemical Engineering
University of Tennessee
Knoxville, Tennessee 37996-2200

H. D. Cochran
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6224

ABSTRACT

A new experimental technique is described in which dynamic processes on surfaces — adsorption, desorption, and diffusion — can be monitored directly. The shift in frequency of resonant surface vibrations in a crystal is monitored as a function of time while the surface is exposed to a time dependent driving force. This surface acoustic wave (SAW) device is capable of resolving changes in surface concentrations of less than 1% of a monolayer over time spans of milliseconds or longer, under pressure conditions ranging from ultra-high vacuum to moderate-to-high pressure. The development of the SAW as a monitor for dynamic processes will help meet the instrumental needs for studying the fluid-solid interfaces which control many separation processes.

INTRODUCTION

In any type of separation the interactions occurring at the interface, or surface, are very important. These surface phenomena occur with mass transfer across a phase, such as adsorption, desorption, crystallization and diffusion. Currently, many of the techniques used to study these surface processes require high-vacuum conditions which are difficult to produce and greatly removed from the actual process conditions.

Some of the techniques currently used to study surface catalysis and phenomena, such as X-ray photoelectron, Auger electron and ion-scaling spectroscopy, provide quantitative analysis of

surface layers and detect impurities on the surface. All of these techniques, however, must be carried out under vacuum conditions and suffer from low resolution (1). Infrared spectroscopy and surface-enhanced Raman spectroscopy may be applied at nonvacuum conditions to measure the amount of material adsorbed on the surface and in some cases may be used to study the rate at which certain surface processes occur. Reflection spectroscopy provides a marginal sensitivity for static adsorption studies but appears to be inadequate for studying rates of surface phenomena (2).

A technique is described in this paper for measuring static and dynamic adsorption on a solid using a SAW device which appears to be suitable for use at elevated pressure. A SAW device consists of a piezoelectric crystal with two pairs of electrodes. A radio frequency (RF) voltage is imposed on one pair of electrodes which induces a surface vibration that propagates across the surface, inducing an RF voltage in a second pair of electrodes. The use of a SAW device allows detection of the quantity of mass adsorbed and the rate of adsorption. This technique should be applicable to many different systems at a variety of temperatures and pressures. The development of the SAW device as a monitor for dynamic processes will help provide much needed instrumentation for studying the fluid-solid interfaces which dominate many separation processes.

The effects of temperature and pressure on the performance of the SAW device will be considered, and the projected sensitivity of the device for static and dynamic measurements will be described. The proposed assembly of the mass detection unit and resonant circuits will be described and applications in the current research program delineated.

THEORY

A simple SAW transducer is a piezoelectric solid onto which interdigital transducers (IDTs) have been applied by coating the solid with a thin metal and subsequently etching it with a photolithographic technique. Upon application of an RF voltage to one IDT, a Rayleigh wave is generated on the surface of the solid by mechanical deformation of the solid from the piezoelectric effect. A second IDT acts as a receiver of the energy traveling across the solid. The process is depicted schematically in Fig. 1. The configuration and the number of IDTs lithographed upon the piezoelectric solid (Fig. 2) determine the resonant frequency of the surface wave and the bandwidth, respectively (3).

When the propagated surface waves interact with adsorbed matter, the wave properties — amplitude, phase, velocity, and frequency — are altered. Wohltjen and Dessy (4) have shown that monitoring the changes in SAW velocity (by measuring frequency

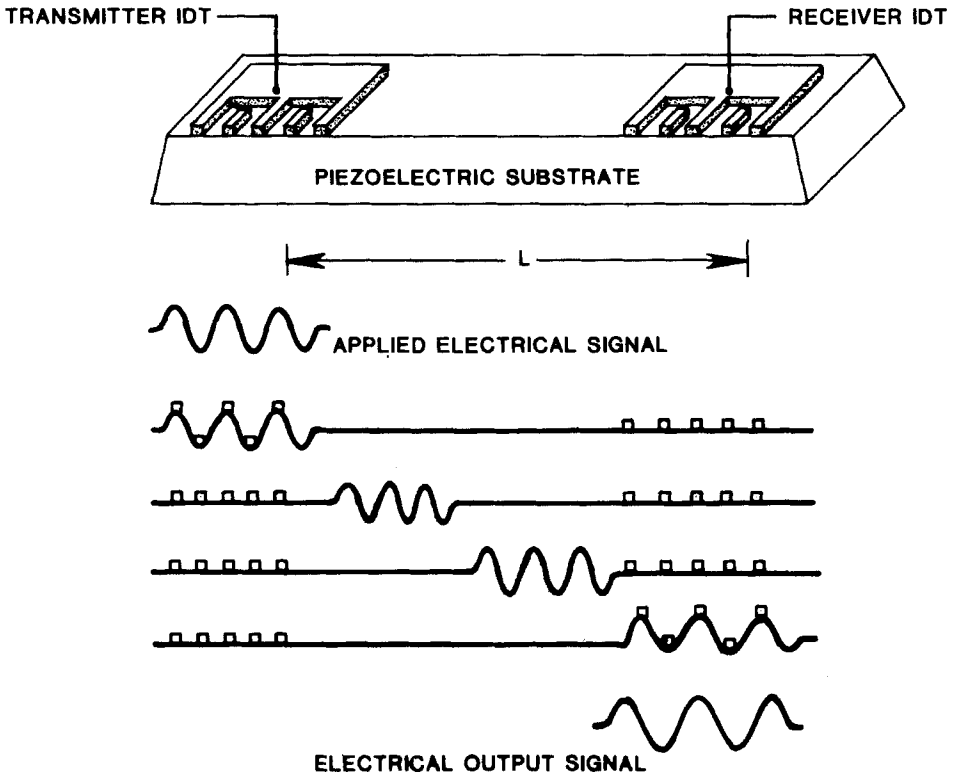
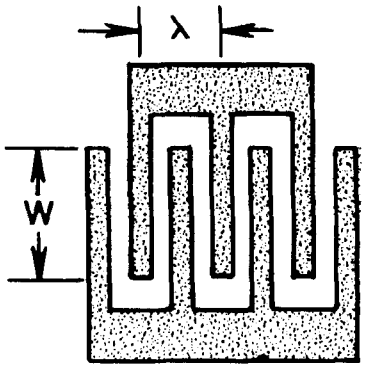


Fig. 1. Schematic diagram showing the propagation of a surface acoustic wave on a piezoelectric crystal.

perturbations) can be much more precise than measuring of amplitude or phase change because of the accuracy attainable in frequency measurements (5).

Many types of materials exhibit piezoelectric qualities. Typically, quartz or lithium niobate crystals are used because of their availability, low cost, good piezoelectric coupling, and low temperature coefficient of delay. Different crystalline orientations will exhibit one or more, but not all, of these advantages (3).



INTERDIGITAL ELECTRODES

Fig. 2. SAW interdigital transducer design.

Sauerbrey (6) developed a relationship between the mass of a thin film deposited on the surface of a piezoelectric quartz crystal (bulk wave rather than surface wave oscillator) and the change in frequency occurring because of this deposition (6). King (5) reported this as:

$$\Delta f = 2.3 \cdot 10^6 f^2 W/A \quad , \tag{1}$$

where

Δf = the frequency change due to the coating,
f = frequency of the quartz plate,
W = weight of film deposit, and
A = area of the electrode.

Electrode spacing determines wavelength and hence operation frequency

$$\lambda = \frac{V_o}{f_o} \frac{\text{(Surface Wave Velocity)}}{\text{(Synchronous Frequency)}}$$

(N) Number of electrode pairs determines bandwidth

$$N = (\%\ \text{bandwidth})^{-1} = \frac{f_o}{\Delta f}$$

Wohltjen later reported a similar relationship for SAW devices with very thin, nonconducting, isotropic overlay films. This relationship was developed from Auld's description of the perturbation analysis of a SAW device (7). Auld's original equation is

$$\frac{\Delta V_R}{V_R} = \frac{-V_R h}{4P_R}\left[\rho'\left|\nu_{Ry}\right|^2 + \left(\rho' - \left(\frac{4\mu'}{V_R^2}\right)\left(\frac{\lambda' + \mu'}{\lambda + 2\mu}\right)\right)\left|\nu_{Rz}\right|^2\right]_{y=0} \qquad (2)$$

where

h = film thickness,
V_R = Rayleigh wave velocity,
ρ' = film mass density,
λ' = Lame' const.,
μ' = shear modules,

$\frac{(\nu_{Ry})_{y=0}}{\sqrt{P_R}}$ = normalized particle velocity components at the surface, and

$\frac{(\nu_{Rz})_{y=0}}{\sqrt{P_R}}$ = normalized particle velocity components at the surface.

With several simplifying assumptions, this becomes

$$\Delta f = (k_1 + k_2)\, f^2\, h\, \rho' \quad , \qquad (3)$$

where

k_1 and k_2 = material constants for the SAW substrate,
Δf = the change in resonant frequency due to perturbation by the overlay film, and
$h\ p'$ = the mass per unit area on the coating film.

Wohltjen (3) has shown that for a YX quartz SAW delay line oscillator this equation is

$$\Delta f = 1.36 \cdot 10^6 f^2 W/A \quad . \qquad (4)$$

Since the resonant frequency of the SAW device may be easily 20 to 200 times greater than the bulk wave frequency and in both devices $\Delta f \propto f^2$, the SAW device is potentially much more sensitive (3).

EXPERIMENTAL

In order to assess the potential of the SAW device for measuring adsorption and desorption rates, equipment must be assembled for determining the frequency change in surface waves propagating across a SAW device and separating out the effects due to surface loading on the crystal from other factors which may influence the frequency. An experimental program must be developed for calibration of the SAW device and for compensation for the effects of pressure and temperature on the frequency measurements. A reference SAW will be used to compensate for many of the perturbations induced by temperature and pressure changes.

Description of Equipment

The SAW device is so small and easily fabricated that many of the problems associated with temperature and pressure changes may be alleviated by using a reference SAW in-line with the experimental SAW. Temperature changes affect the frequency shift observed due to mass loading in three ways: (1) expansion of the crystal at high temperature (8), (2) temperature effects on the resonant circuit, and (3) a reduction of the quantity of material adsorbed due to greater kinetic energy.

Expansion of the solid may be minimized by judicious choice of the solid (for example, AT quartz has a temperature coefficient of nearly zero up to temperatures of 45°C) or by compensation with a reference SAW maintained at the same temperature (8). Drift of Δf due to electronic components in the resonant circuit may also be minimized by careful selection of components and by enclosing both the reference and experimental SAWs in a constant temperature chamber. Careful design of the SAW delay line and its amplifier is essential in minimizing noise and maintaining a high system quality factor (3). The effects of increased kinetic energy of the adsorbing gases and hence less adsorption are among the fundamental phenomena of adsorption kinetics which will be studied with the SAW device.

Pressure effects may be considered as follows: First, an increase in pressure causes emission of a compressional wave from the solid onto the surrounding fluid and contributes to the wave's attenuation (4). The shift in frequency due to the pressure effect is positive and may be eliminated by calibration with a nonadsorbing gas like helium (9). Second, energy loss to the vapor will increase with density resulting in a drift in frequency. This perturbation of the resonant frequency is primarily due to the coupling of the surface wave to the compressional longitudinal sound waves in the gas. The magnitude of this frequency shift is related to the compressibility and sonic velocity of the surrounding gas and can be corrected for quantitatively by calibration with a nonadsorbing gas. Schoenwald has shown that various gases at fixed pressures yield different frequency shifts, hence the frequency shift is not due to mechanical distortion of the solid (9).

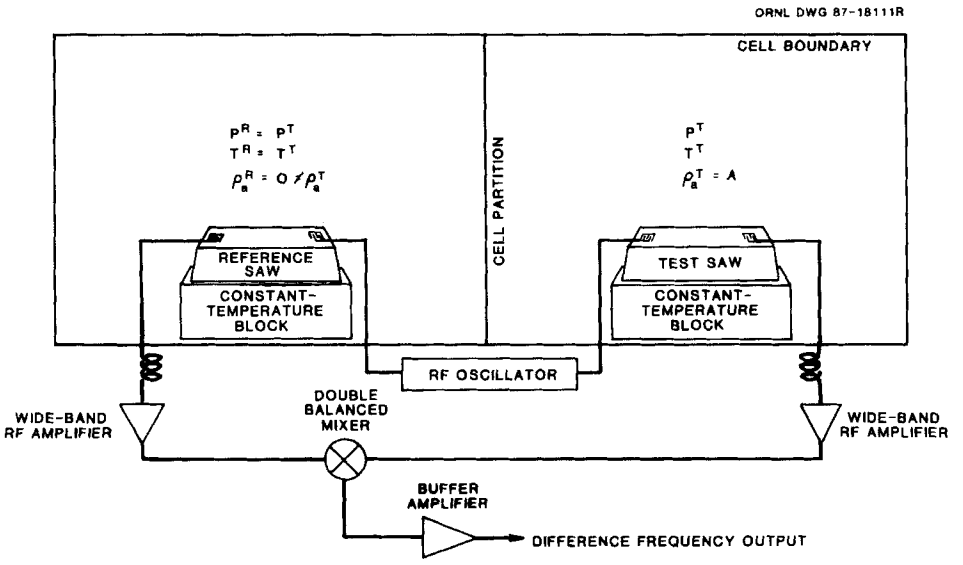


Fig. 3. Schematic diagram of the experimental SAW device.

Two identical SAW devices will be used, and the frequencies of the two delay lines will be mixed to yield a difference frequency which is related solely to the mass loading on the experimental SAW. Figure 3 presents a schematic representation of our experimental apparatus. Wohltjen has shown that a 3 GHz SAW device with a 1.0 cm^2 area can detect a mass change of 3×10^{-11} g. This precision should allow detection of <1.0% of a monolayer. With modifications in crystal size and the number of IDTs, the sensitivity of this device may be further increased.

Our experimental apparatus uses a Hewlett-Packard model 5315B frequency counter capable of measuring ±10 Hz at 10^8 Hz in 1 s. This precision may be increased by a factor of ten with the addition of one component, allowing measurements of ±1 Hz at 10^8 over 1 s with a corresponding increase in the sensitivity of adsorption and desorption rates. The reference surface can be balanced against the experimental SAW to within the precision of the frequency counter. The reference SAW can be maintained at a temperature within ±0.1 °K of the experimental SAW and a total system pressure within ±0.1% from 10^{-7} torr to 200 bar.

SUMMARY

Potentially, the SAW device should have greater accuracy than the Cahn balance, for static measurements and with a much wider operating range of temperatures and pressures. For dynamic measurements at pressure above vacuum conditions the SAW will be unique. Potential applications are as a detector for gas and liquid chromatography and possibly as a means for detecting supercritical fluid solubilities in flow experiments (5,10,11).

ACKNOWLEDGMENTS

This work has been supported by the Chemical Sciences Division, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc., and subcontract with the University of Tennessee. The authors would also like to thank Paul Fisher for his contributions.

REFERENCES

1. Carberry, J. J., and A. Varma, Chemical Reaction and Reactor Engineering, Marcel Dekker, New York, 1987, pp. 151-238.

2. Borovkov, V. Y., and V. B. Kazansku, Russian Journal of Physical Chemistry 59(2), 196 (1985).

3. Wohltjen, H., Sensors and Actuators 5, 307 (1984).

4. Wohltjen, H., and R. Dessy, Anal. Chem. 51(9), 1459 (1979).

5. King, W. H., Jr., Anal. Chem. 36(9), 1735 (1964).

6. Sauerbrey, G., Z. Physik. 155, 206 (1959).

7. Auld, B. A., Acoustic Fields and Waves in Solids, 2 Ch. 2 (1973).

8. Kahn, G. M., The Review of Scientific Instruments 43(1), 447 (1972).

9. Schoenwald, J. S., A. B. Harker, W. W. Ho, J. Wise, and E. J. Staples, 1980 Ultrasonics Symposium, 193 (1980).

10. Konash, P. L., and G. J. Bastlaans, Anal. Chem. 52, 1929 (1980).

11. Wohltjen, H., and R. Dessy, Anal. Chem. 51(9), 1465 (1979).