An accurate and versatile vibrating capacitor for surface and adsorption studies

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An accurate and versatile vibrating capacitor for surface and adsorption studies

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Abstract The analysis of the desirable features of a vibrating-capacitor probe for adsorption studies and the disturbing effects which hinder their realisation has led to the construction of a set-up which combines low noise and drift, good reproducibility even after movement of the sample, and a low time constant. It is particularly suited for kinetic measurements in adsorption studies for which it is practical to provide direct differentiation of the output; it can also be used for accurate measurements of absolute contact potential differences.

1 Introduction

One of the oldest and most used methods for the investigation of interactions between gases and solid surfaces is the measurement of the change in the electronic work function of the surface upon coverage with an adsorbed layer (Gundry and Tompkins 1968, Rivière 1969). In line with the present trend towards multimethod investigations, it is rarely used as the only method today but, combined with other surface-sensitive methods, it can provide important additional information. Also, once the exact correlation between the change in work function and the coverage is established, it can be used for very well resolved monitoring of coverages and their variation with time. An accurate, disturbance-free device for continuous measurement of the contact potential $\Delta\phi$ of the surfaces of single crystals is important for such applications.

Of the various possibilities for measuring the contact potential the Kelvin–Zisman method (Kelvin 1898, Zisman 1932, also called the vibrating-capacitor method) has the advantages that the surface under investigation is not influenced in any way and that it averages linearly over possible inhomogeneities. The problems, caused by stray capacitances, which can arise in its application have been treated extensively before (Surplice and D'Arcy 1970, de Boer et al 1973). Also, efforts have been made to minimise (Blott and Lee 1969, Surplice and D'Arcy 1970, Danyluk 1972, de Boer et al 1973) or to eliminate completely (Craig and Radeka 1970) the influence of stray capacitances and to make the drive of the vibrating capacitor easier to handle and more reliable (Besocke and Berger 1976). Despite these improvements which have been made over the last few years, we do not know of a report of a vibrating capacitor which combines as many properties of

importance to surface studies as possible. In the following, we first outline these properties and then describe how they have been realised in a vibrating capacitor constructed and used in our laboratory.

2 Necessary properties of a vibrating capacitor for surface studies

2.1 General properties

A vibrating capacitor for surface studies must, of course, be UHV-compatible, i.e. bakeable, and should be operated in a self-compensating way via feedback of the lock-in output (Palevsky et al 1947). Both conditions are easily fulfilled. Furthermore, it is desirable to locate the whole drive mechanism inside the vacuum chamber to minimise the mobile masses (thus permitting high frequencies which are of advantage as will be discussed below, and making effective shielding easy), and to make demounting for bake-out unnecessary. Also, it will be shown that an interior drive mechanism is best suited for minimisation and compensation of stray capacitances. This placement of the drive is easy with a piezoelectric drive (Besocke and Berger 1976), but a conventional soft-iron drive is possible as well and has in fact been used here. For measurements of the kinetics of adsorption and desorption, the reference electrode, which of necessity has to be placed close to the sample surface, must not shield the sample from the gas flux. This has been accomplished very elegantly with a pendulum device by Hölzl and Schrammen (1976). Reference electrodes made of a high-transparency grid mounted on a thin wire loop of a sufficiently small size to avoid edge effects (Tracy and Palmberg 1969) and covered with an inert substance (e.g. SnO_2) to make the work function stable have also been used successfully (Delchar and Tompkins 1967, Tompkins 1967, Gundry and Tompkins 1968).

Many surface investigations demand direct accurate regulation (e.g. by the current passed through the sample) and measurement (e.g. by a thermocouple attached to it) of the sample temperature. This means that the very sensitive preamplifier has to be connected to the vibrating reference electrode instead of to the sample; otherwise the heater power supply and the temperature measurement devices would have to be extremely well isolated from ground, and free of hum and noise. Also, if a preamplifier with a high input resistance is used, the large capacitances of the electronics connected to the sample would greatly decrease the input signal. In our experience, it is quite simple to connect the self-compensating circuitry to the vibrating reference electrode (see also Tracy and Palmberg 1969), which takes care of all these difficulties and makes possible the connection of any number of ungrounded electronic apparatuses to the sample.

It is of great advantage to make the reference of small mass and let it vibrate at as high frequency as possible. This eliminates uncontrollable coupling of vibration to other parts of the system which can considerably disturb the measurements. The smaller contribution from $1/f$ noise, and the complete elimination of disturbances by environmental vibrations (e.g. by knocking against the vacuum system), if high frequencies are used, add to the stability of the measurements. An additiona advantage of higher frequencies is the increase of input signal with frequency. In order to utilise fully this increase, a current-sensitive instead of a voltage-sensitive preamplifier has to be used (see below). A high vibration frequency would also appear to be of importance for good time resolution in kinetic experiments. Usually, however, the vibration frequency is not the limiting factor here, but some electronic time constant. The possibility to move and reposition the sample relative to the reference electrode without degrading the accuracy of the $\Delta\phi$ measurement is mandatory for the determination of absolute

contact potentials (i.e. of the difference of work function between two samples, which can then be used to arrive at the absolute work function of one sample, if that of the other is known), and is desirable for many applications of $\Delta\phi$ measurements. The latter is, for instance, the case if the sample is to be removed for cleaning or dosing with gas, and to be repositioned afterwards without losing the reference to the previous measurement. Also, the exact position of the sample can change during heating by thermal expansion of the mounting. It is desirable, therefore, that the reading is essentially independent of the exact sample position. This can be achieved if the influence of stray capacitances is eliminated. As shown below, a special screening and nulling procedure can fulfil this purpose.

As for all sensitive circuitry, the signal/noise ratio of the detector circuit has to be high and the drift and time constants must be low. Good design of the mechanical and electronic systems makes these characteristics possible.

2.2 Stray capacitances and the current amplifier

We examine an arrangement in which all parts of the vibrating electrode, with the exception of the reference electrode proper, are surrounded by a static screening with adjustable potential U_A. This produces three capacitances which change periodically with the drive frequency and therefore contribute measurable currents in the detector circuit. These are: the capacitance C between the sample and the reference electrode (contact potential $\Delta\phi$), the (small) stray capacitance C_S between the reference electrode and the walls of the vacuum system (contact potential $\Delta\phi_S$), and the capacitance C_A between the vibrating electrode and the screening (contact potential $\Delta\phi_A$). If a current amplifier is connected to the reference electrode, the output (with signal U) of the lock-in amplifier is connected to the sample, and the adjustable voltage U_A is put on the screening, the result can be represented by the equivalent circuit of figure 1. The charge on the reference electrode which is changing due to vibration is

$$Q = C(\Delta\phi + U) + C_A(\Delta\phi_A + U_A) + C_S\Delta\phi_S. \tag{1}$$
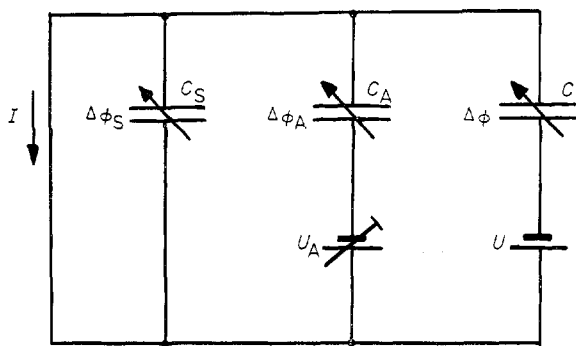
Figure 1 Equivalent circuit of the Kelvin probe with the periodically changing capacitances C between the sample and the reference electrode, C_A between the screening and the vibrating electrode and C_S between the walls of the vacuum system and the reference electrode. The contact potentials $\Delta\phi$, $\Delta\phi_A$ and $\Delta\phi_S$ are acting at these capacitances. The output voltage U of the lock-in amplifier is applied to the sample and the adjustable voltage U_A to the screening. The current I caused by changes in the capacitances flows through the current-sensitive preamplifier.

The current in the preamplifier is

$$I = \mathrm{d}Q/\mathrm{d}t = (\Delta\phi + U)\dot{C} + (\Delta\phi_A + U_A)\dot{C}_A + \Delta\phi\dot{C}_S \tag{2}$$

where the $\dot{C}_X$ are the time derivatives of the capacitances. In the balanced state, $I = 0$ and the output voltage of the lock-in amplifier is given by

$$U = -\Delta\phi - [(\Delta\phi_A + U_A)\dot{C}_{A\text{RMS}}\cos\beta + \Delta\phi_S\dot{C}_{S\text{RMS}}\cos\gamma]/\dot{C}_{\text{RMS}}$$

$$= -\Delta\phi - B/\dot{C}_{\text{RMS}} \tag{3}$$

where the $\dot{C}_{X\text{RMS}}$, the RMS values of the time derivatives of the capacitances, are effective here because of the rectifying and averaging action of the lock-in amplifier; β and γ are the phase angles.

Equation (3) shows that it is desirable to make the sum B zero for contact potential measurements and to at least keep it constant for measurements of changes in the work functions. As small changes in $\dot{C}$ cannot always be avoided even if the amplitude of vibration stays constant, it is preferable to fulfil the condition $B \approx 0$ even for measurements of work function changes. If no screening is provided, $\Delta\phi_S$ has to be compensated by an additional potential on the vibrating electrode. This can be done in principle, but leads to rather complicated electronic provisions, and the use of a current-sensitive amplifier would become very difficult. It is easier to make the sum B equal to zero by suitable choice of U_A. This is achieved satisfactorily if the change in the indicated contact potential produced by a realistic change of $\dot{C}$ (by a change of the mean distance between the sample and the reference electrode) is sufficiently small. In addition, $\Delta\phi_A$ and $\Delta\phi_S$ have to stay constant during adsorption experiments. This can be achieved by coating the screening and vibrating electrode with SnO_2. The influence of small changes in $\Delta\phi_S$ by ad- or desorption on the walls of the vacuum vessel is greatly reduced by the screening. Changes in C_A and C_S, caused by changes in the sample–reference distance, can certainly be neglected. If the sum B has been made equal to zero, it is seen from equation (2) that the signal in the preamplifier is proportional to $\dot{C}$. To a first approximation the capacitance C is given by (Gundry and Tompkins 1968)

$$C = \epsilon_0 A/(S_0 + S\sin\omega t) \tag{4}$$

where A is the area of the reference electrode, S_0 is the mean distance between the reference electrode and the sample, and S is the amplitude and ω the angular frequency of vibration. Differentiation of equation (4) leads to

$$\dot{C} = C[S\omega\cos\omega t/(S_0 + S\sin\omega t)]. \tag{5}$$

Therefore the peak signal current in the preamplifier is proportional to the capacitance between the sample and the reference electrode, the fractional displacement of the reference electrode and the frequency of the vibrator. This does not mean, however, that the input signal rises linearly with frequency if a voltage-sensitive preamplifier is used. Normally, the input resistance of the preamplifier will be made larger than the impedance $1/(\omega C_p)$ of the parasitic capacitances C_p which lie across the input of the preamplifier and thus determine the input signal. If the vibrator frequency is increased in order to increase the signal current I, this decreases the parasitic AC resistance and the input signal does not increase with frequency as expected. However, if a current-sensitive preamplifier is used, whose input resistance is considerably smaller than the shunt impedance, the input signal indeed rises linearly with frequency.

3 Experimental realisation

3.1 *Mechanical*

In order to keep the stray capacitance small compared with the screening capacitance, the vibrating electrode has to be as small as possible and well screened. The chosen configuration of the vibrator with drive is shown in figure 2. The drive
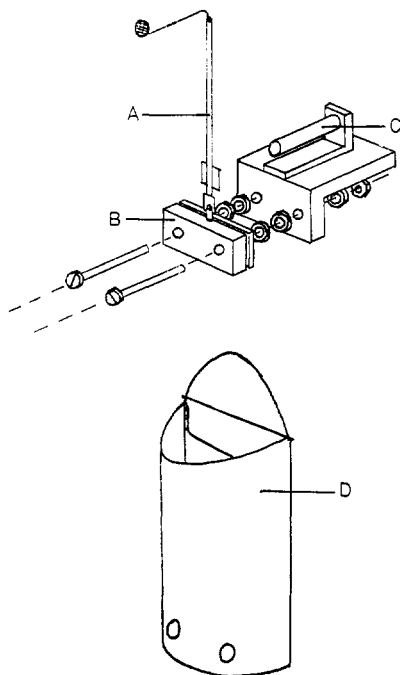
Figure 2 Principal mechanical arrangement of the Kelvin probe. A and B are the reference electrode assembly with Mumetal platelet and holder. C is the soft-iron piece around which several layers of anodically oxidised aluminium wire have to be wound. The screening D is slid over the holder B and all parts are fixed to the base plate with screws and alumina washers.

consists of a U-shaped soft-iron piece, around which several layers of anodically oxidised aluminium wire have been wound. A Mumetal platelet, spot-welded to a thin stainless steel tube, is situated opposite the open part of the U. The tubing is supported in a holder by a metal plate and a pin. The reference electrode proper is fixed to the upper end of the tubing. It consists of a 3–4 mm wide ring of thin molybdenum wire, covered with a high-transparency (80%) stainless steel grid. The screening which surrounds the whole assembly, consisting of vibrator and holder, and screens it against the drive and most of the environment, consists of stainless steel sheet. The vibrating electrode, screening and soft-iron slug are electrically isolated from each other. The vibrating electrode and screening have been covered with SnO_2 by exposure to $SnCl_2$ followed by heating. The electrical signals are transmitted via rigid, isolated, partly screened leads which are free of microphonics, to the vacuum leadthroughs. The fundamental frequency of the vibrator is around 160 Hz. Normally, however, the vibrator is driven in the first overtone, which was found at about 1150 Hz, in agreement with expectance. The resonance at the overtone is found to be quite sharp (less than 0·5 Hz), so that difficulties are caused by small changes in the frequency of the drive oscillator. The vibrator is driven, therefore, by a quartz oscillator (10 MHz) which is followed by an adjustable divider.

This simple arrangement keeps the oscillator and vibrator in phase for days. The vibrator amplitude is about 0·1 mm, and

the distance between sample and reference is usually set between 0·5 and 0·3 mm.

3.2 *Electronics*

The preamplifier is a normal current amplifier using the IC AD515L with a feedback resistor of 10^{10} Ω. The extremely low offset and bias values of this IC make all adjustments unnecessary. The rest of the circuit with the lock-in amplifier and feedback conforms to the normal, well known arrangement. The only additional provision is for compensation of the stray signal at f_0 (the drive frequency) which couples from the drive to the signal lead despite screening and which would overload the lock-in. As the signal frequency is at $2f_0$ because of the soft-iron drive, the stray signal at f_0 can be totally compensated using the circuit of figure 3, leaving only the true vibrator signal at $2f_0$.
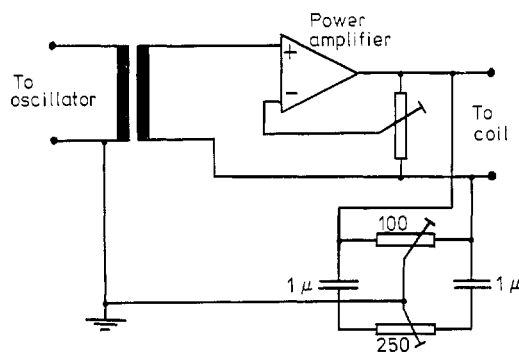
Figure 3 Circuit diagram for the compensation of the stray signal at f_0.

4 Properties of the apparatus

The following properties were obtained with the damping time constant of the lock-in set at 100 s, with 6 dB/octave roll-off. (This time constant is *not* the effective time constant of the system, since it is drastically decreased by the high closed-loop gain.) The noise at the output as recorded with a fast x/t recorder was routinely below $\pm 0\cdot5$ mV$_{RMS}$; the drift was always below 1 mV h^{-1} (see figure 4). The dynamic response
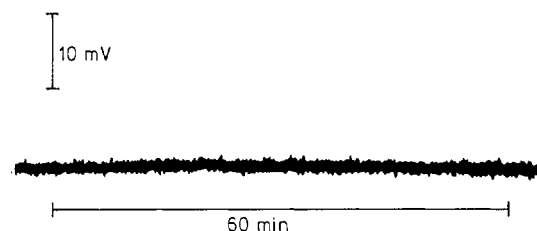
Figure 4 Illustration of the drift and noise levels (less than 1 mV h^{-1} and $\pm 0\cdot5$ mV$_{RMS}$ respectively).

was tested by imposing a stepwise increase of 600 mV on the potential difference between the sample and the reference. Figure 5 shows the response of the output signal as recorded by an oscilloscope. The time constant for adjustment to $1/e$ of the disturbance is 20 ms; 99% is reached in less than 100 ms. The closed-loop gain is about 10^3, so the deviation of the measured from the real change in work function is negligible for adsorption and desorption. With optimal adjustment of the screening potential U_A, the indicated contact potential difference for an increase in the sample–reference distance of 1 mm is about 2–3 mV. A measured contact potential difference is
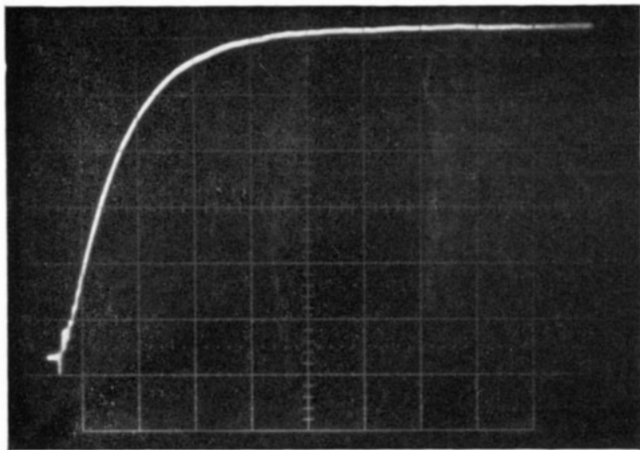
Figure 5 Dynamical response to a stepwise increase of 600 mV in the potential difference between the sample and the reference. The time constant for adjustment to 1/e is 20 ms and 99% of the final value is reached in less than 100 ms. Vertical scale 100 mV/division; horizontal scale 20 ms/division. Other conditions are as in figure 4.

reproduced to ± 1–2 mV after movement of the sample in the system and after it has stood for one day.

For kinetic measurements via the change in $\Delta\phi$ (e.g. for continuous measurements of the sticking coefficient, or for temperature-programmed or isothermal desorption) it is of advantage to provide for direct electronic differentiation of the $\Delta\phi$ output. If the correlation between $\Delta\phi$ and the coverage is then known sufficiently well, direct plots of rates (of adsorption or desorption) against coverage are possible. This principle has been used before (Engelhardt and Menzel 1976) with a less elaborate vibrator. The use of the apparatus described above (Pfnür *et al* 1977), combined with a better time response and much lower noise through active filtering (Feulner *et al* 1977), can considerably improve such measurements. As an example, figure 6 shows a comparison of desorption spectra (rate of
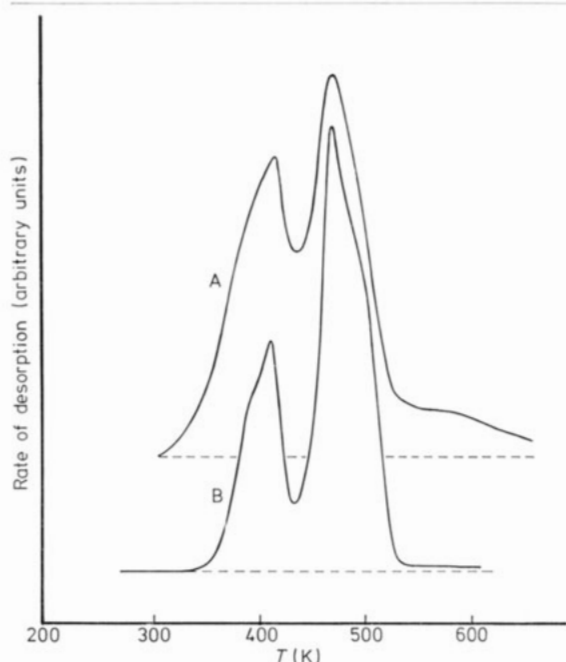

Figure 6 Temperature-programmed desorption spectra for CO on Ru (001), obtained by monitoring the pressure change (Δp, curve A) and the time derivative of the change in work function ($\Delta\phi$, curve B). Heating rate 5 K s⁻¹.

desorption as a function of surface temperature obtained by temperature programming) for CO on Ru(001), taken via the pressure change (conventional 'flash desorption') and via differentiation of the change in work function using the vibrator described here. It can be seen that the resolution of the latter is much better and that the background caused by desorption from the crystal support and edges is eliminated. The increased resolution enables a much more detailed kinetic analysis to be made (see Pfnür *et al* 1977).

5 Summary

The set-up for a vibrating capacitor described here has been developed on the basis of an analysis of the requirements of a versatile instrument for surface investigations. It is fully UHV-compatible and easy to handle. Electronic supplies and measuring devices can be connected to the sample without changing the properties of the circuitry. The influences of noise, drift and stray capacitances are so small that they can be neglected for all practical purposes, and absolute contact potential differences can be measured. The transparent, inert reference electrode and the small system time constant make possible the recording of fast changes in the work function caused by adsorption and desorption. This mode of operation is made easy by direct coupling to a differentiating device, thus allowing the direct measurement of rate of adsorption or desorption as a function of coverage for systems where the functional dependence of the change in work function upon the coverage is known.

References

Besocke K and Berger S 1976 *Rev. Sci. Instrum.* **47** 840–2

Blott B H and Lee T J 1969 *J. Phys. E: Sci. Instrum.* **2** 785–8

de Boer J S W, Krusemeyer H J and Burhoven Jaspers N C 1973 *Rev. Sci. Instrum.* **44** 1003–8

Craig P P and Radeka V 1970 *Rev. Sci. Instrum.* **41** 258–64

Danyluk S 1972 *J. Phys. E: Sci. Instrum.* **5** 478–80

Delchar T A and Tompkins F C 1967 *Proc. R. Soc.* A **300** 141–58

Engelhardt H A and Menzel D 1976 *Surf. Sci.* **57** 591–618

Feulner P, Engelhardt H A and Menzel D 1977 to be published

Gundry P M and Tompkins F C 1968 *Experimental Methods in Catalytic Research*, ed R B Anderson (New York: Academic)

Hölzl J and Schrammen P 1974 *Appl. Phys.* **3** 353–7

Kelvin (Lord) 1898 *Phil. Mag.* **46** 82–120

Palevsky H, Swank R K and Grenchik R 1947 *Rev. Sci. Instrum.* **18** 298–314

Pfnür A, Engelhardt H A and Menzel D 1977 to be published

Rivière J C 1969 *Solid State Surface Science* vol 1, ed M Green (New York: Dekker)

Surplice N A and D'Arcy R J 1970 *J. Phys. E: Sci. Instrum.* **3** 477–82

Tompkins F C 1967 *The Solid–Gas Interface* vol 2, ed E A Flood (New York: Dekker)

Tracy J C and Palmberg P W 1969 *J. Chem. Phys.* **51** 4852–62

Zisman W A 1932 *Rev. Sci. Instrum.* **3** 367–8