CHEMISTRY LETTERS, pp. 1763-1766, 1985.

THE FREQUENCY DEPENDENCE OF MOTT-SCHOTTKY PLOTS

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The charging current of the space charge layer of a CdS(0001)/aq. KCl junction was measured by Time Domain Spectroscopy in the short time region. The relaxation spectrum consists of a multitude of exponentials, which is interpreted by a heterogeneous semiconductor surface. This explains the dependence of conventional Mott Schottky plots on frequency and resulting errors in the determination of flatband potential and donor density.

Two of the fundamental properties of semiconductors are their donor density N_d and their flatband potential U_{fb}. They can be evaluated in theory through the use of the Mott Schottky equation,[1)] if the corresponding area A is known:

$$C^{-2}=\left(\frac{2}{qN_d\kappa\varepsilon_o A^2}\right)\left(U_b-U_{fb}-\frac{k{\times}T}{q}\right) \tag{1}$$

Thus, a plot of the squared inverse differential space charge capacity C^{-2} versus bias potential U_b should yield a straight line. In practice, however, this line is usually dependent on the frequency of the measuring system and the nature of the electrolyte. This introduces different flatband potentials and different donor densities for every new frequency used.[2)] Since the donor density and the flatband potential are also known from other experiments and are theoretically independent of the measuring frequency, this phenomenon is known as the Mott Schottky data dispersion and has been an obstacle in practical photoelectrochemistry for the last 25 years.

The semiconductor-electrolyte interface can be represented by a single series RC-element, if the interface is uniform (i.e. the relaxation spectrum should be mono-exponential). It is however doubtful if the interface is really uniform, and we propose a different circuit, which assumes area-dependent surface properties of the crystal (space charge capacity and resistance to this capacity at the interface and in the bulk), as shown in Fig. 1.

By the use of a new experimental technique, Time Domain Spectroscopy (TDS), see Fig. 2, we are able to measure the impedance of an electrochemical cell in the time region between 1 s and 10 ns. This corresponds to frequencies up to 50 MHz. The cell impedance is given by the equation:

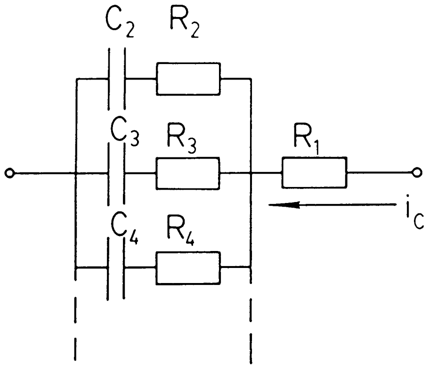

Fig. 1. The equivalent circuit for the interface. R_1 is the sum of all series resistances (solution, contacts, etc.), and the RC-elements represent the local space charge capacity and resistance (interface and bulk).

$$Z_C = Z_0/\bar{a} \qquad ; \ \bar{a}=(U_0-U_r)/(U_0+U_r) \qquad (2)$$

where U_0 and U_r are original and reflected signal, respectively. Since current and resistance are inversely proportional, a plot of $\bar{a}$ versus t is proportional to a plot of i_C versus t.

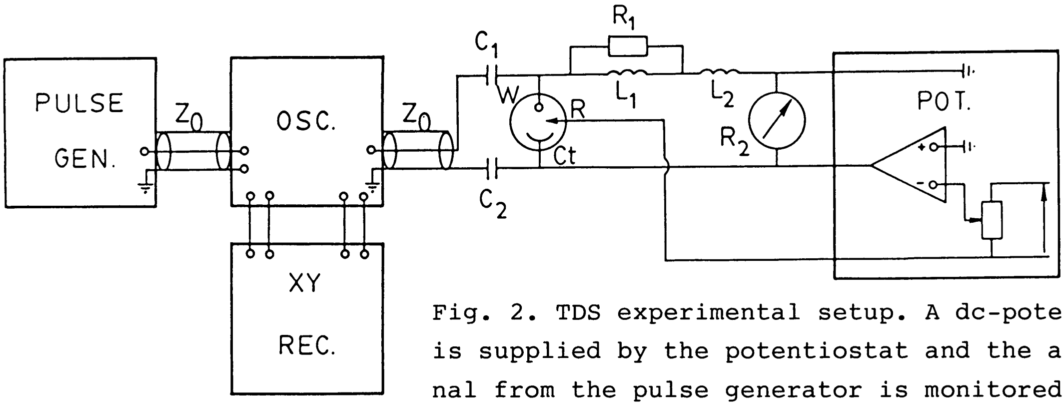

Fig. 2. TDS experimental setup. A dc-potential is supplied by the potentiostat and the ac-signal from the pulse generator is monitored on the oscilloscope.

A CdS single crystal (0001) was cut, mounted and etched (final etch in 30% HCl) in the usual manner. For a junction of this crystal in contact with a 0.5 M (1 M = 1 mol dm^{-3}) aq. KCl solution, we measured the TDS spectrum and calculated $\bar{a}(t) \sim i_C(t)$. Figure 3 then shows a plot of ln $\bar{a}$ versus time. Instead of observing a straight line, as expected for a uniform surface with a single relaxation time, we see that the current i_C contains several superposed exponentials.

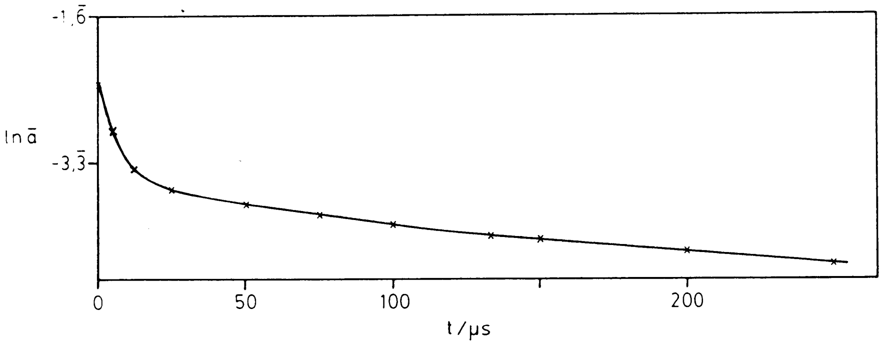

Fig. 3. The logarithm of the coefficient $\bar{a} \sim i_C$ versus time.

This is similar to results obtained with the ZnO/electrolyte junction.[3)] By graphical analysis, the different exponentials could be evaluated and be transformed into the elements of the equivalent circuit in Fig. 1. A change in one of the chemical parameters of the system (i.e. the electrolyte or oxygen concentration in solution) was then found to generally influence only one or a defined subset of these elements.

Furthermore, a series of measurements of these elements in function of bias potential allows the establishment of a simultaneous Mott Schottky plot for the different exponentials, as shown in Fig. 4. The different lines in Fig. 4 are now each frequency-independent. The use of Eq. 1 requires the knowledge of either the donor density or the relative surface area, in order to calculate the other quantity from the slope of Fig. 4. Since it is unlikely that the donor density has different discrete values (instead of a continuous spectrum), we assumed it constant (equal to the value obtained from the Hall potential) and calculated the areas corresponding to the different slopes. These areas were each considerably less than the total geometric area (usually between 10 and 40%) and the sum of all areas also slightly less than the total area. We therefore concluded that the single exponential contributions in Fig. 3, characterized by their relaxation time and amplitude, pertain to different geometric areas of the interface with different electronic properties.

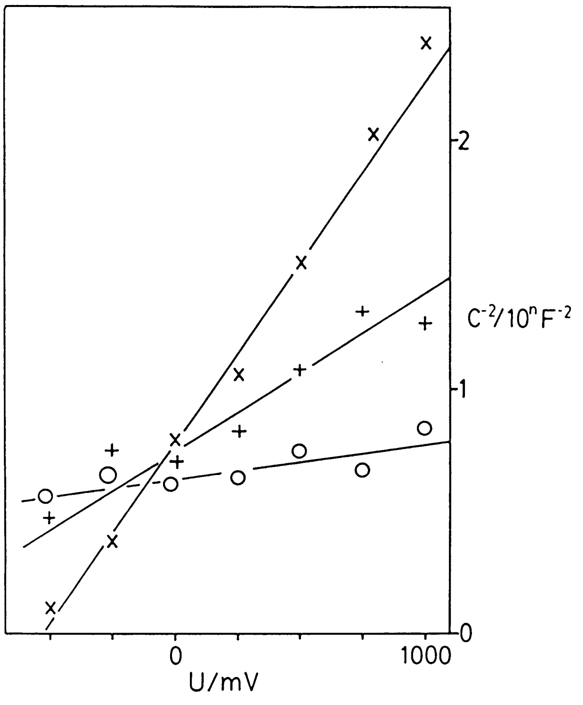

Fig. 4. A typical simultaneous Mott Schottky plot. Details vary greatly with surface preparation. Exponent n = 16, 17, 17 for x, + and o, respectively.

Since our experiment is limited in time resolution, we anticipate the existence of more exponentials at shorter times, which would account for the missing area in the above calculation. If the sum of all areas would be considerably greater than the total geometric area, this would indicate that the donor density is not constant over the crystal surface. However, so far no proof in this direction has been found.

The multi-exponential relaxation spectrum of the interface has been observed for all junctions investigated (ZnO, CdS) and the relative distribution is generally a function of electrode preparation and electrolyte. We therefore assume the general applicability of the above results on other junctions as well and draw the following conclusions on the origin of data dispersion observable with the use of the Mott Schottky equation:

a) The relaxation time (or the real and imaginary resistances R and X in the case of frequency measurements) of the total space charge capacity current is a function of time (or frequency), as seen in Fig. 3. The measurement at different frequencies will therefore lead to different values of the space charge capacity and consequently introduces a first data dispersion.

The critical frequency, below which the result is frequency independent, is at the onset of the second slowest exponential. Because of the solution resistance R_1 (see appendix in Ref. 3) there is, however, a certain interdependence amongst all exponentials and the critical frequency does not depend on the faster exponentials alone.

b) The donor density and the flatband potential of a given semiconductor can be determined through the direct use of Eq. 1 only for a totally homogeneous interface. In all other cases the area corresponding to a measured impedance is less than the total geometric area. The use of a measured impedance (or relaxation time) with a non-corresponding area results in a second type of data scattering. However, in the case of constant donor density, we can obtain the area distribution as outlined above.

c) Semiconductor surfaces in the mm^2 region are not uniform. The differences in crystal surface orientation, defects, oxidized layers, etc. and the consequent regio-selective chemisorption of solution species (surface states) produce a locally different electronic contact. The variation in effective surface charge results in a Fermi level distribution (entailing a flatband level distribution) and differences in effective interface distance produce different interface resistances.

The electronic contact at the interface, as observable through the measurement of the cell impedance, is therefore a function of the crystal, the surface preparation technique, the solvent-electrolyte system, as well as a function of contact time. This is the reason for a third kind of data scattering.

A comparison with some reports in the literature[4-6] on the variation of Mott Schottky data shows that usually one of the above three reasons is implied and we believe that the assumption of a heterogeneous interface is more plausible than the explanations offered so far.

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(Received September 4, 1985)