

Semiconductor Electrodes

XXIII. The Determination of Flatband Potentials from Differential Stress Measurements with Attached Piezoelectric Detectors

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ABSTRACT

A new method for the determination of the flatband potential, V_{fb} , of semiconductor electrodes by differential stress measurements of a piezoelectric detector bonded to the semiconductor is reported. Values of V_{fb} for single crystal n-SrTiO₃ and p-GaAs, and polycrystalline n-TiO₂ in 1N NaOH and 1N H₂SO₄ are shown to be in good agreement with previously determined values. Possible application of such measurements to the study of surface changes and breakdown is suggested.

The flatband potential, V_{fb} , of a semiconductor/electrolyte solution interface is an important parameter in explaining the electrochemical characteristics of the system in the dark and under illumination (1-3). V_{fb} is a function of both the semiconductor material and the solution composition, and is measured to determine the locations of the semiconductor valence and conduction bandedges with respect to solution energy levels. Usually V_{fb} -values are determined by direct measurements of the space charge differential capacity, C_{sc} , (Schottky-Mott plots) or by determinations of the open-circuit photopotential (or the potential for the onset of the photocurrent) under intense irradiation. Both of these methods often suffer from difficulties which result in large uncertainties in the V_{fb} -values estimated by them. In C_{sc} measurements the Schottky-Mott plots are frequently nonlinear and yield V_{fb} -values which are functions of the frequency used. This has been attributed to the effect of surface states and other factors (4). The estimation from photopotentials can also be perturbed by the existence of surface states or intermediate levels as well as by recombination effects which, for an n-type semiconductor, will yield onset photopotentials less negative than the actual V_{fb} -value (5).

V_{fb} can also be determined by observing the voltametric response in the dark of couples spanning a potential range above and below V_{fb} (5, 6). Such measurements usually yield a V_{fb} -value with considerable uncertainty and may also be perturbed by electron transfers occurring via surface states. In this paper, we

propose a method for the determination of V_{fb} , based on the measurement of differential stress (with a piezoelectric crystal attached to the semiconductor electrode) as a function of potential, which is experimentally simple and theoretically direct.

There have been several previous reports of the application of piezoelectric materials (which are materials which produce a potential when placed under a stress) to measurements at metal electrodes (7-10).

From a modified form of the Lipmann equation that was used by Gokhstein (7) for metal electrodes, the differential surface stress ($\partial\sigma_s/\partial E$) is related to the surface charge density (q) and deformation by

$$\partial\sigma_s/\partial E = -q - \partial q/\partial\theta \quad [1]$$

where θ is the ratio of the surface area before and after deformation. For an ideally polarized electrode, the term $\partial q/\partial\theta$ is zero, since the charge density does not depend upon the deformation of the electrode surface. Even for nonpolarizable electrodes this term may be small and is equal to zero at the flatband potential, because at V_{fb} there is no charge on the electrode.

For semiconductor electrodes, the excess charge q is distributed in the space charge region. At potentials negative of the flatband potential, the space charge region has an excess of electrons and the differential stress measurements will be positive. At the flatband potential there is no excess charge and the differential stress is zero. For potentials positive of the flatband potential there is an accumulation of holes in the space charge region and the differential stress will be negative. Thus, as implied by Eq. [1], the differential stress tracks the space charge, and the intercept of the dif-

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differential stress as a function of potential will be at the flatband potential.

Experimental

The experimental technique used for semiconductor electrodes is the same as the technique developed for metal electrodes (8-10). Three electrodes were prepared by bonding a ceramic piezoelectric disk (Edo Western Corporation, Salt Lake City, Utah) to the back of the semiconductor with Devcon 5-minute epoxy cement. The piezoelectric disk was electrically insulated from the semiconductor and the electrolyte with silicone cement (Fig. 1). The face next to the semiconductor was maintained at ground potential to insure that a-c potentials on the semiconductor would not affect the potential measured across the piezoelectric disk.

The three semiconductors studied were single crystal n-type SrTiO_3 (2 mm thick), which had been reduced in hydrogen at 800°C for 5 hr; single crystal p-type GaAs (1 mm thick), which was doped with Zn; and polycrystalline n- TiO_2 (0.2 mm thick), which was prepared by oxidizing titanium foil in an open flame. The electrolytes used were stock solutions of 1N NaOH and 1N H_2SO_4 .

The measurement procedure generally followed that used with metal electrodes (8-10). An a-c modulating signal superimposed on a potential ramp generated the piezoelectric signal (see Fig. 2). For this experiment both the in-phase ($\phi = 0^\circ$) and quadrature ($\phi = 90^\circ$) piezoelectric signals were recorded simultaneously for each potential scan.

Results and Discussion

Separation of quadrature and in-phase signals.—If the semiconductor/electrolyte interface is represented as an equivalent circuit composed of a resistor and capacitor in series (where the resistor represents the bulk resistance of the semiconductor and the capacitance is that of the space charge region), then the a-c modulation voltage will produce two components of electrode stress. The first, attributable to the IR heating caused by the a-c current that flows through the bulk of the semiconductor, is proportional to the potential difference across the bulk resistance. It will be in-phase and proportional to the modulating signal amplitude. The second is due to the surface stress caused by a change in the charge density in the space charge region. This component is proportional to the potential difference across the space charge capacitance and will be 90° out of phase with, but still proportional to, the modulating signal. The assumption has been made that $\omega RC \gg 1$, so that $\tan^{-1}(\omega RC) \sim 90^\circ$. All of the data supports this assumption. This proportionality of the in-phase and quadrature signals to the modulating signal amplitude is shown in Fig. 3. Under these conditions, the in-phase signal is about an order of magnitude larger than the quadrature signal.

The determination of flatband potentials.—The in-phase signal should always have the same sign at all electrode potentials while the quadrature signal should change sign at the flatband potential. This is shown in Fig. 4 for n- SrTiO_3 . At very positive potentials ($\sim +11\text{V}$) the quadrature signal again changes sign, probably because of a breakdown phenomenon since this potential corresponds to the onset of d-c anodic current.

The quadrature signals near the flatband potentials for n- SrTiO_3 and n- TiO_2 in 1N H_2SO_4 and 1N NaOH are shown in Fig. 5 and 6. The V_{fb} -values determined from such differential stress measurements are listed in Table I. These results agree very well with values previously reported (3, 11, 12) and have an uncertainty of only ± 25 mV or less, which is better than the usual methods for determining flatband potentials. The pH shift for these materials is near 59 mV/pH unit, as expected (3, 11, 12).

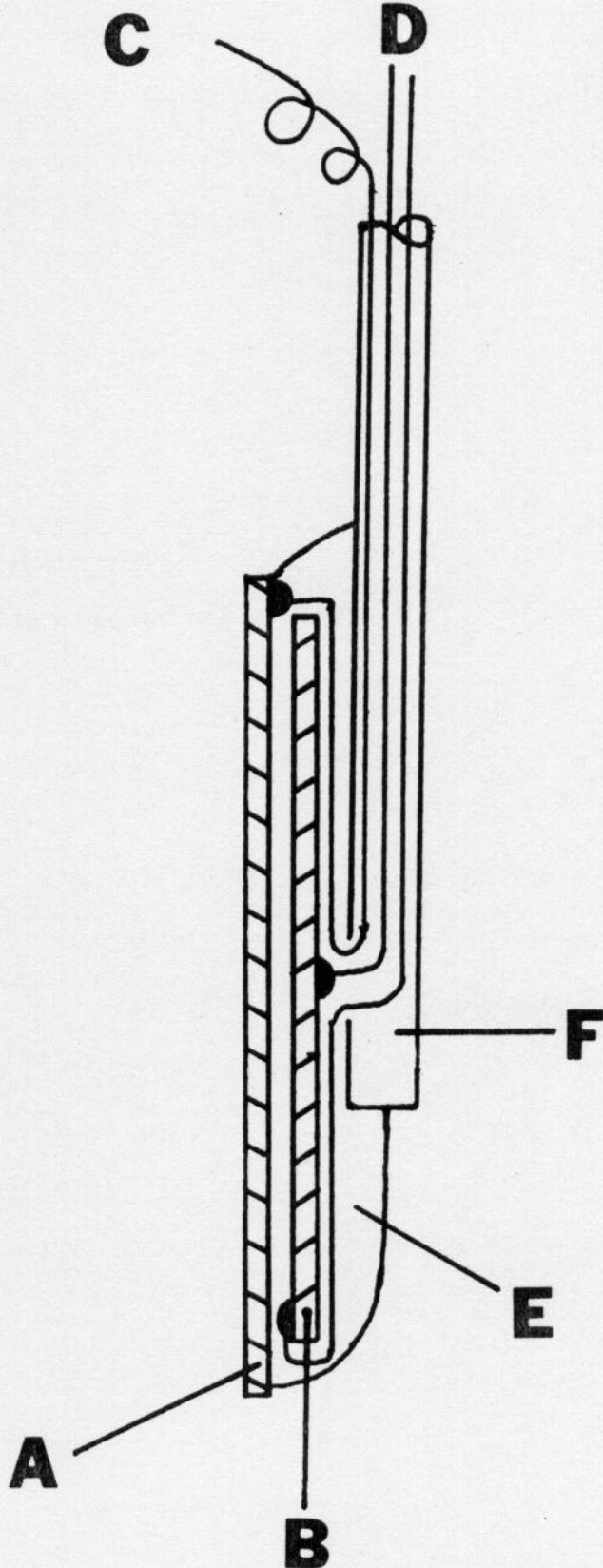


Fig. 1. The working electrode. A: semiconductor; B: piezoelectric ceramic disk ($\phi = 16$ mm; thickness = 0.2 mm); C: lead to potentiostat; D: leads from piezoelectric to lock-in amplifier pre-amplifier; E: epoxy cement; F: Pyrex glass tube.

Frequency dependence.—The frequency dependence of the differential stress measurements is shown in Fig. 7 for the quadrature signal at three different frequencies and in Fig. 8 for the in-phase signal at the

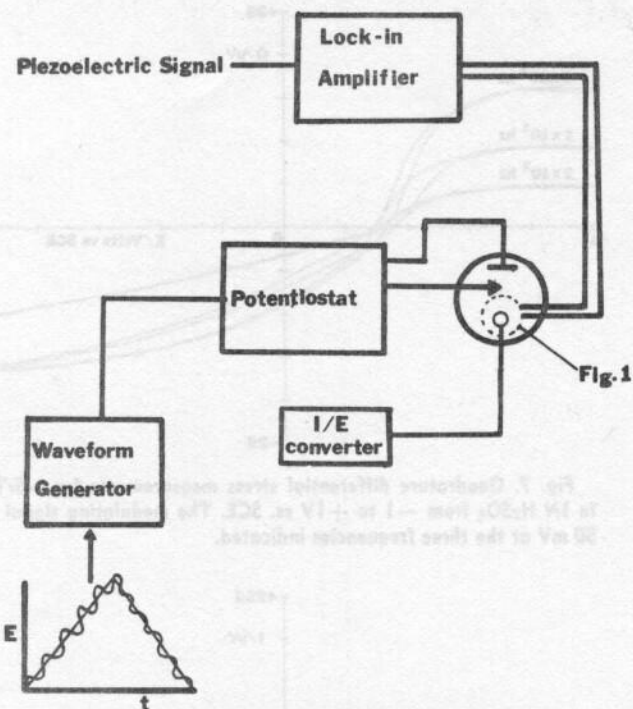
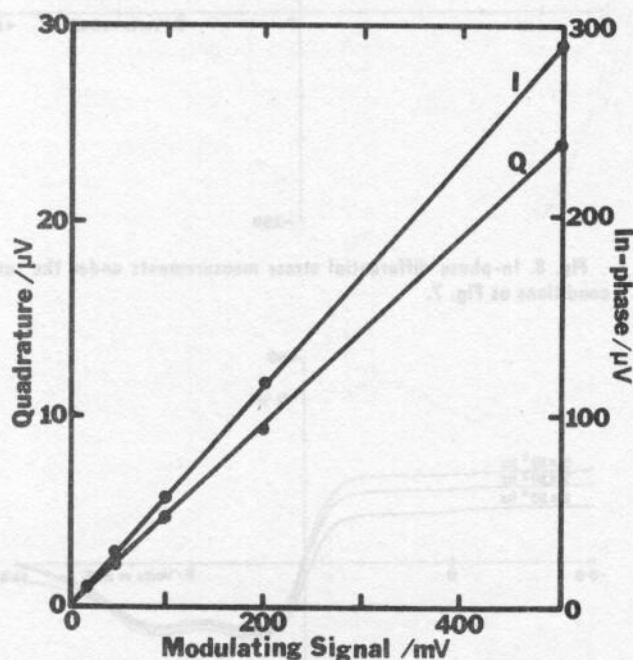


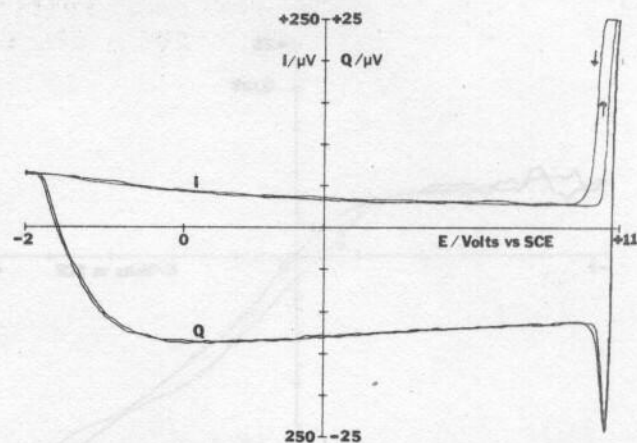
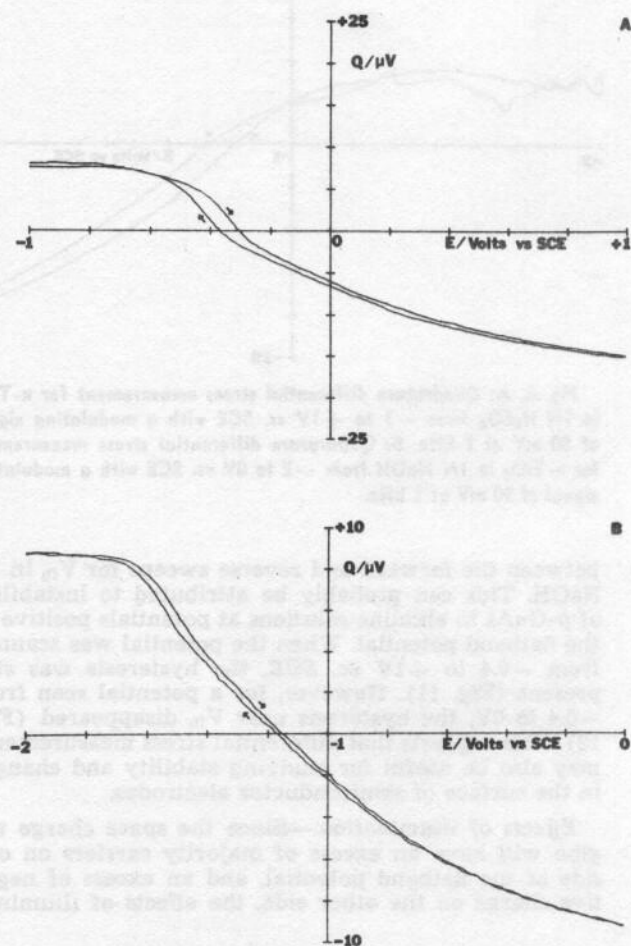
Fig. 2. Block diagram of the apparatus

Fig. 3. (A) In-phase and (B) quadrature differential stress measurements for n-SrTiO₃ in 1N NaOH at 0V vs. SCE with a modulating frequency of 1 kHz.

same three frequencies for n-SrTiO₃ in 1N H₂SO₄. The capacitive impedance of the space charge region increases with a decrease in frequency, therefore, increasing the absolute value of the quadrature signal at potentials other than the flatband potential. The intercepts for all three frequencies are within a range of 40 mV. Since the IR stress (in-phase) signal is an order of magnitude larger than the space charge (quadrature) signal, the changes in the quadrature signal have only a small effect on the in-phase signal.

Effects of chemical changes at the electrode surface.

—The quadrature differential stress measurements for p-GaAs are shown in Fig. 9 and 10 for 1N H₂SO₄ and 1N NaOH, respectively. The extent of frequency de-

Fig. 4. In-phase (*I*) and quadrature (*Q*) differential stress signals for n-SrTiO₃ in 1N NaOH for cyclic potential sweep from -2 to +11V vs. SCE at 20 mV/sec with a modulating signal of 50 mV at 1 kHz. The in-phase signal scale is an order of magnitude larger than that for the quadrature signal.Fig. 5. A: Quadrature differential stress measurement for n-SrTiO₃ in 1N H₂SO₄ from -1 to +1V vs. SCE with a modulating signal of 50 mV at 1 kHz. B: Quadrature differential stress measurement for n-SrTiO₃ in 1N NaOH from -2 to 0V vs. SCE with a modulating signal of 50 mV at 1 kHz.

pendence of intercept was similar to that for n-SrTiO₃. The V_{fb} -values, listed in Table I, are in reasonable agreement with previous measurements (13). An interesting point to note is the difference in hysteresis for p-GaAs for the acidic and alkaline electrolytes when the potential is scanned between +1.5 and -0.5V vs. SCE. The data for 1N H₂SO₄ show almost no hysteresis, while there is approximately 0.1V difference

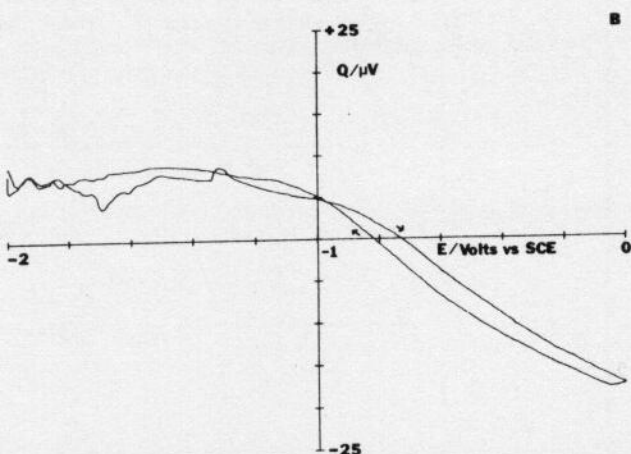
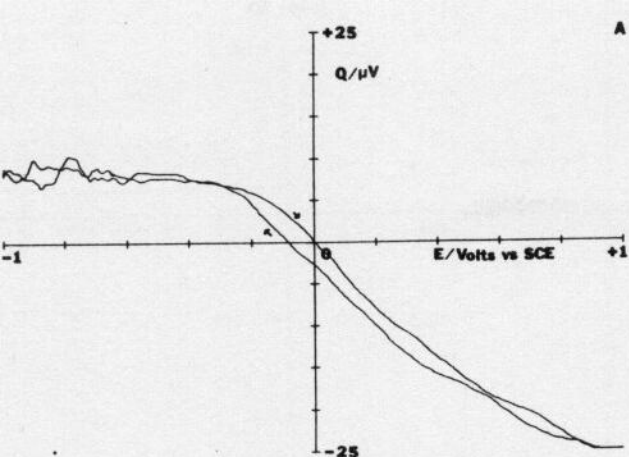


Fig. 6. A: Quadrature differential stress measurement for n-TiO₂ in 1N H₂SO₄ from -1 to +1V vs. SCE with a modulating signal of 50 mV at 1 kHz. B: Quadrature differential stress measurement for n-TiO₂ in 1N NaOH from -2 to 0V vs. SCE with a modulating signal of 50 mV at 1 kHz.

between the forward and reverse sweeps for V_{fb} in 1N NaOH. This can probably be attributed to instability of p-GaAs in alkaline solutions at potentials positive of the flatband potential. When the potential was scanned from -0.4 to +1V vs. SCE, the hysteresis was still present (Fig. 11). However, for a potential scan from -0.4 to 0V, the hysteresis near V_{fb} disappeared (Fig. 12). This suggests that differential stress measurements may also be useful for studying stability and changes in the surface of semiconductor electrodes.

Effects of illumination.—Since the space charge region will have an excess of majority carriers on one side of the flatband potential, and an excess of negative charge on the other side, the effects of illumina-

Table I. Comparison of V_{fb} -values obtained by differential stress measurements to previously reported results.

| Semiconductor | Electrolyte | This work | | Previous measurements | |
|----------------------|-----------------------------------|----------------------|-----------------|-----------------------|-----------|
| | | V_{fb} (V vs. SCE) | pH ^a | V_{fb} (V vs. SCE) | Reference |
| n-SrTiO ₃ | 1N H ₂ SO ₄ | -0.35 | 0.0 | -0.30 | (11) |
| | 1N NaOH | -1.15 | 13.3 | -1.19 | (3) |
| | | | 13.5 | -1.10 | (11) |
| n-TiO ₂ | 1N H ₂ SO ₄ | -0.05 | 0.0 | -0.01 | (11, 14) |
| | 1N NaOH | -0.80 | 13.3 | -0.90 | (3, 12) |
| | | | 13.5 | -0.80 | (11, 14) |
| p-GaAs | 1N H ₂ SO ₄ | 0.5 | 2.1 | 0.10 | (13) |
| | 1N NaOH | -0.30 | 9.2 | -0.24 | (13) |

^a As reported or estimated to ± 0.1 pH unit.

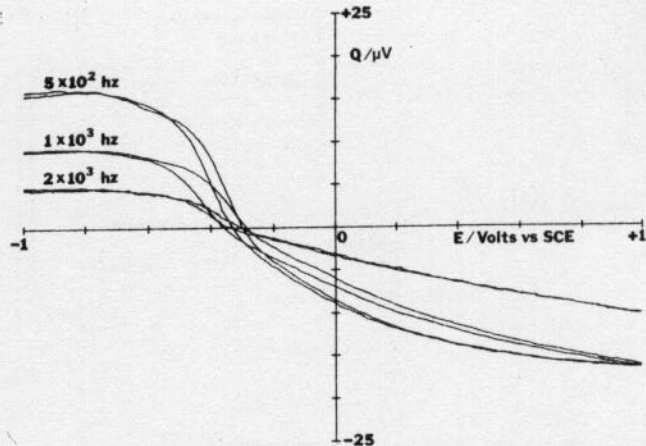


Fig. 7. Quadrature differential stress measurements for n-SrTiO₃ in 1N H₂SO₄ from -1 to +1V vs. SCE. The modulating signal was 50 mV at the three frequencies indicated.

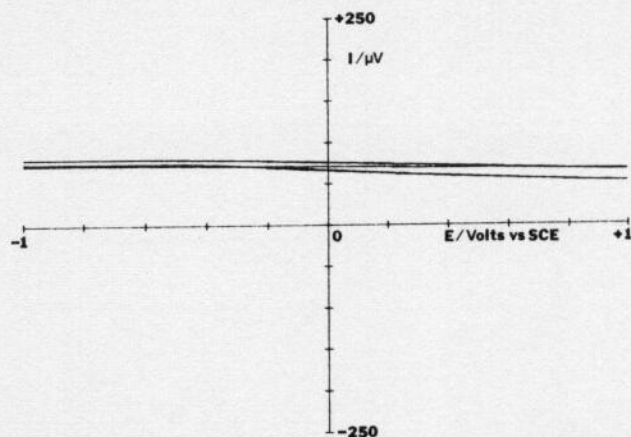


Fig. 8. In-phase differential stress measurements under the same conditions as Fig. 7.

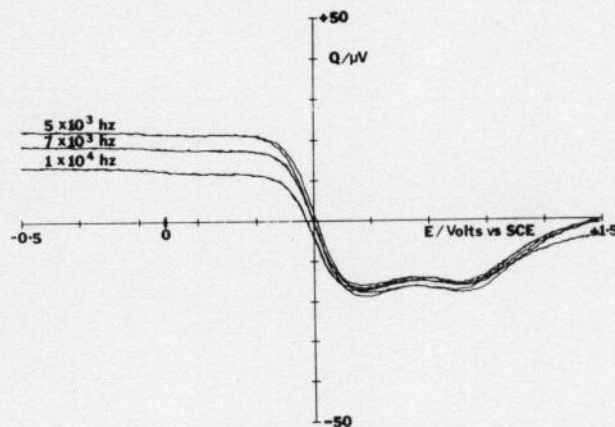


Fig. 9. Quadrature differential stress measurements for p-GaAs in 1N H₂SO₄ from -0.5 to +1.5V vs. SCE. The modulating signal was 50 mV at the three frequencies indicated.

tion should be different for potentials positive and negative of V_{fb} . For p-GaAs at potentials more positive than V_{fb} , there is an accumulation of majority carriers in the space charge region and illumination should not substantially change the differential stress measurements. For potentials negative of V_{fb} the bands are bent downwards, and the effects of illumination should be much larger. The differential stress measurements for p-GaAs in the dark and under

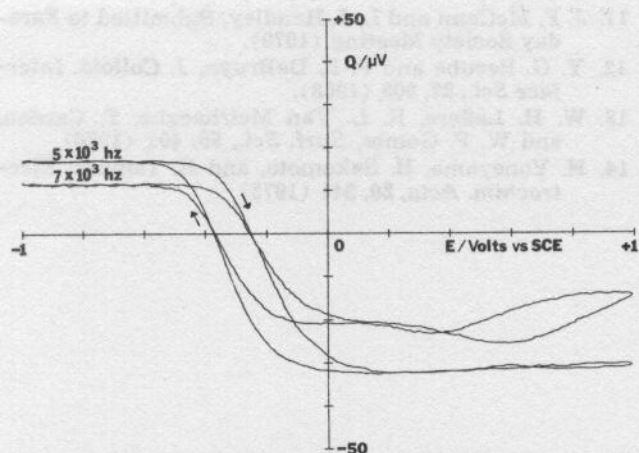


Fig. 10. Quadrature differential stress measurements for p-GaAs in 1N NaOH from -1 to $+1$ V vs. SCE. The modulating signal was 50 mV at the two frequencies indicated.

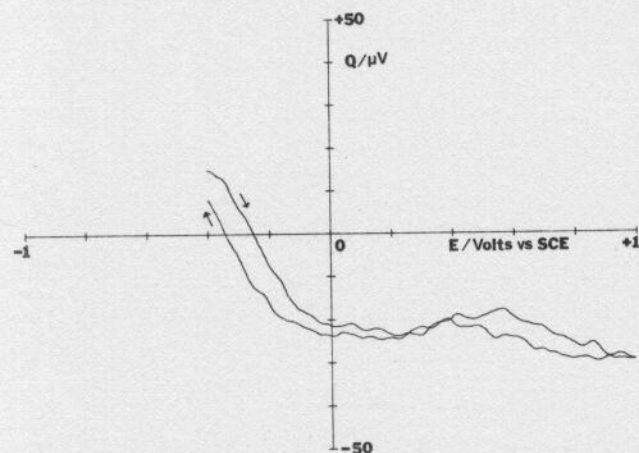


Fig. 11. Quadrature differential stress measurements for p-GaAs in 1N NaOH from -0.4 to $+1$ V vs. SCE with a modulating signal of 50 mV at 5 kHz.

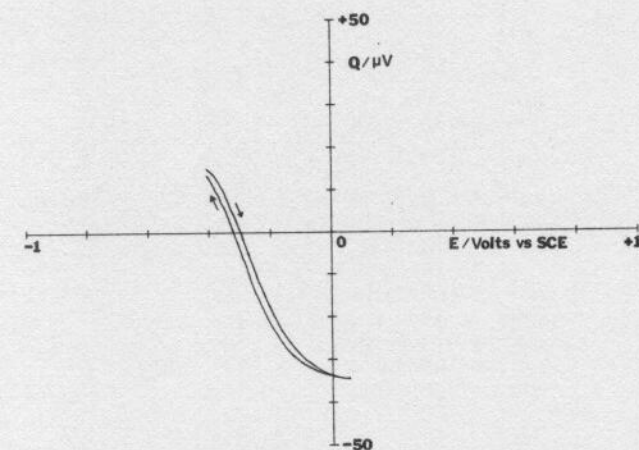


Fig. 12. Quadrature differential stress measurement for p-GaAs in 1N NaOH from -0.4 to 0 V vs. SCE with a modulating signal of 50 mV at 5 kHz.

illumination (Fig. 13) agree with this prediction. The effect of illumination is to decrease the extent of band bending, thereby reducing the surface stress.

Conclusions

Preliminary experiments have demonstrated that V_{fb} -values of both p- and n-type semiconductor electrodes, single crystal and polycrystalline, can be determined from differential stress measurements as a

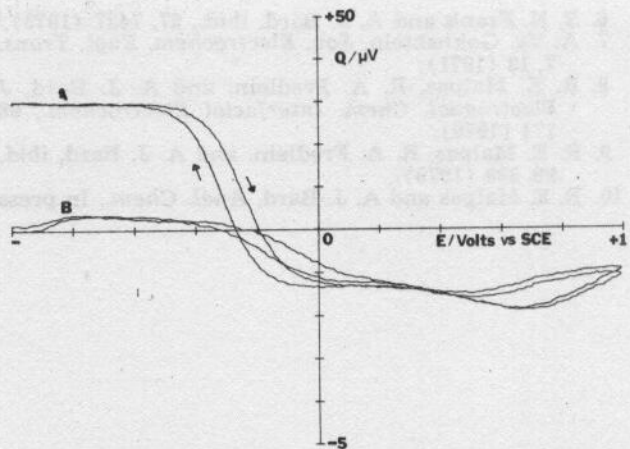


Fig. 13. Quadrature differential stress measurements for p-GaAs in 1N NaOH from $+1$ to -1 V vs. SCE: (A) in dark and (B) under illumination. The modulating signal was 50 mV at 5 kHz.

function of potential. The only assumption that has been made is that a semiconductor electrode can be represented as an equivalent circuit consisting of a resistor and capacitor in series. The V_{fb} -values from the differential stress measurements are in excellent agreement with independent previous measurements and show the expected pH shift of 59 mV/pH unit for n-SrTiO₃ and n-TiO₂.

In addition to determination of V_{fb} , the sharp change in the differential stress observed near the breakdown potential may be of use in elucidating the phenomena occurring in this region. As seen in Fig. 4, the quadrature signal has a sharp minimum near the breakdown potential; there is definite hysteresis in the in-phase signal but none for the quadrature signal. The dependence of the differential stress signals on frequency and illumination is in qualitative agreement with the experimental results. Preliminary results also suggest that differential stress measurements may be useful in studying the stability and changes in the surface of semiconductor electrodes. Work is in progress to obtain a better understanding for these latter effects as well as extending V_{fb} measurements to other semiconductors and other solvent/electrolyte systems.

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