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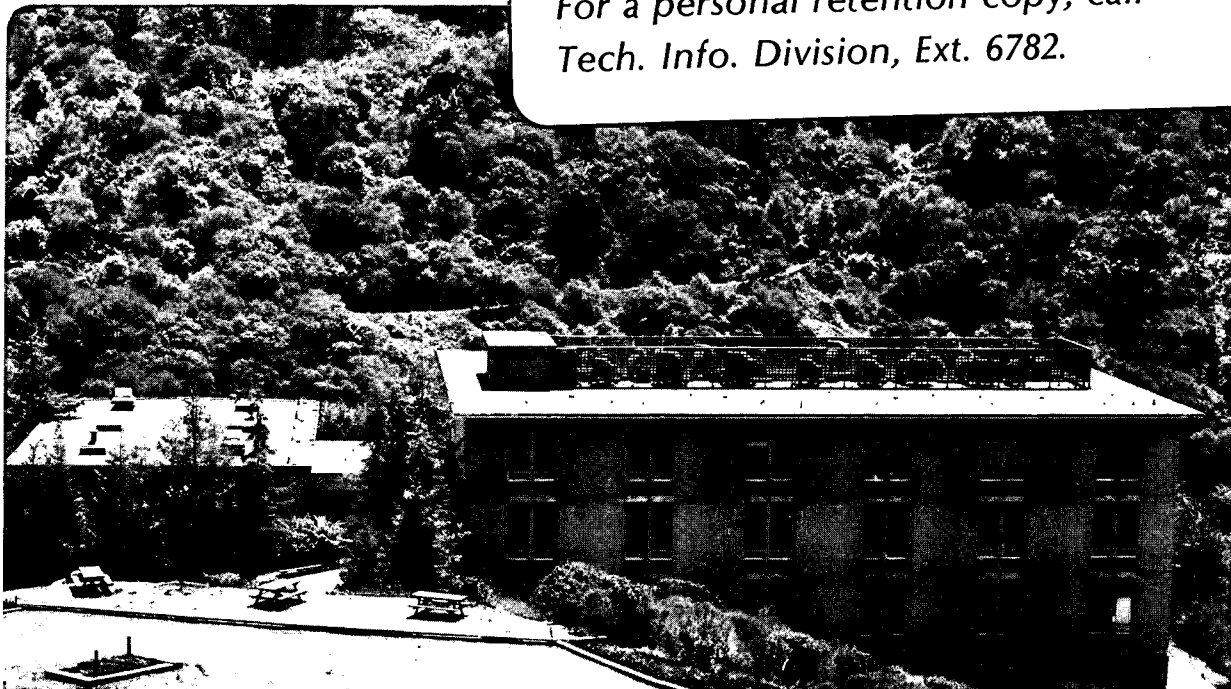
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C.S. Blair and D.W. Hess

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of Carrier Concentrations in Thin Film Photoanodes

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ABSTRACT

Carrier concentrations in thin film iron oxide and titanium oxide photoanodes are determined using a metal/insulator/semiconductor structure. Capacitance-voltage measurements of this structure are distinct from the usual liquid junction impedance measurements, because results of the present study are not dependent upon electrolyte/semiconductor interface properties. Further, determination of the conductivity of the photoanode films permits the calculation of carrier mobilities.

INTRODUCTION

The electrical properties of materials used as liquid junction solar cells ultimately determine their energy conversion efficiency. Two of the most important electrical properties are the flatband potential and the carrier concentration. The carrier concentration is particularly significant since it determines the space charge region thickness and the depth available for light absorption in the semiconductor surface. These properties are usually determined from impedance measurements of the photoelectrochemical cell by plotting $1/C^2$ vs. voltage, thereby generating a Mott-Schottky plot (1).

Experimental difficulties in performing capacitance measurements of solid/liquid interfaces have been previously discussed (2-6). Most of these difficulties involve complex interactions between the semiconductor and the electrolyte. For instance, specific ion adsorption on the semiconductor surface and variation of the Helmholtz layer capacitance with voltage have been suggested as causes of non-linear Mott-Schottky plots and non-Nernstian electrode behavior (2,3). Electrode surface treatments also have a strong influence on Mott-Schottky plot linearity (4). Further, the difficulty of interpreting non-linear Mott-Schottky plots has been addressed (2,5,6). In this paper, a technique capable of measuring semiconductor electrode carrier concentrations without the use of an electrolyte is described.

CAPACITANCE-VOLTAGE TECHNIQUE

Impedance measurements in photoelectrochemical cells are used to ascertain the thickness of the semiconductor space charge or depletion region. In n-type semiconductors, this region is initially formed by the net flow of electrons from the semiconductor into the electrolyte. However,

a depletion region can also be formed merely by applying an electric field across a semiconductor. If a dielectric layer is present on the semiconductor surface, high electric fields can be applied without initiating current flow. This latter structure is called a Metal/Insulator/Semiconductor (MIS) capacitor, and is the basis of many solid state devices.

Capacitance-voltage measurements of the MIS structure represent a well-established diagnostic technique utilized in the fabrication of integrated circuits. The usual goal of MIS measurements is the determination of dielectric properties such as dielectric constant and electronic charge levels in the insulating film. In these investigations, the electrical properties of the semiconductor (usually silicon) are well-known. However, as will be indicated below, electrical properties of the semiconductor can also be obtained. A number of reviews discuss the capacitance-voltage technique in detail (7,8) so only a brief description will be given here.

The total capacitance of the MIS structure is given by the series capacitance of the insulator and the semiconductor.

$$C = 1/C_I + 1/C_{SC} \quad [1]$$

Here, C is the total capacitance, C_I the insulator capacitance, and C_{SC} the semiconductor space charge capacitance.

If a positive potential is applied to a dielectric layer above an n-type semiconductor, majority carriers (electrons) accumulate at or near the semiconductor/insulator interface, giving essentially zero depletion width. In this case, $1/C_{SC}$ is negligible compared to $1/C_I$ and the total capacitance is the insulator capacitance. As the voltage becomes negative, electrons are driven away from the dielectric/semiconductor interface, and a depletion region is formed. This depletion or space charge region presents an additional capacitance in series with the dielectric capacitance (Fig. 1).

As the negative potential is increased, more electrons are repelled from the semiconductor surface, and the depletion region widens, thereby increasing the space charge capacitance, and reducing the overall capacitance due to the series combination given in Eqn. [1]. When sufficiently negative voltages are applied so that minority carriers (holes for an n-type semiconductor) are attracted to the surface, the space charge region has reached its maximum value, and the capacitance remains nearly constant with further increases in potential. Of course, the maximum width of the depletion region is dependent upon the doping level and the dielectric constant of the semiconductor.

The maximum and minimum capacitance values can be used to calculate the charge carrier concentration N , in the semiconductor (7).

$$N = \frac{2\epsilon_I^2 \epsilon_0 \psi}{e d_I^2 \epsilon_s \left(\frac{C_{\max}}{C_{\min}} - 1 \right)} \quad [2]$$

In this expression, ϵ_I and ϵ_s are the dielectric constants of the insulator and the semiconductor respectively, d_I is the dielectric layer thickness, e is the electronic charge, ϵ_0 the permittivity of free space, and ψ is the semiconductor surface potential. The surface potential is the bias required to force the semiconductor into accumulation, where $C = C_{\max}$. The slope of the central portion (depletion region) of the curve is also related to the carrier density by the expression (7):

$$\frac{dC}{dV} = C^3 \frac{\epsilon_I}{\epsilon_s e N d_I^2} \quad [3]$$

which upon integration becomes:

$$\left(\frac{C_I}{C} \right)^2 = \frac{2C_I^2}{\epsilon_s e N} (V - V_0) + 1 \quad [4]$$

In Eqn. [4], V_0 is a constant which accounts for interface and/or insulator charges. Naturally, this expression is similar to the usual Mott-Schottky relation, but V_0 is not related to the electrolyte dependent flatband potential. Thus, the CV technique conveys no information about the semiconductor flatband potential. Fortunately, this is not a serious problem, since the flatband potential can be determined with reasonable accuracy by other techniques (9).

EXPERIMENTAL

All photoelectrodes analyzed in this study were deposited thin films. Iron oxide films were deposited onto iron substrates (Puratronic Foil, Alfa Products) by the rf glow discharge enhanced reaction of iron pentacarbonyl and oxygen (10). Substrate temperatures ranged from 350–500°C and plasma power densities were .079 to 0.4 watts/cm². Under these conditions, α -Fe₂O₃ was the only phase detected by X-ray diffraction in the polycrystalline films. Further, in all cases, film densities were approximately 90% of the theoretical density. Titanium dioxide films were deposited on titanium substrates by a similar glow discharge process using titanium tetrachloride and oxygen as gas phase reactants (11).

MIS structures were produced by electron beam evaporation (the Temescal electron gun was operated at 7KV and 400 mA) of a layer (500–3000Å) of quartz on top of the metal oxide films. Electrical contact was made by evaporating aluminum dots (0.46 mm²) onto the quartz film through a shadow mask.

A schematic of the C-V measurement system is shown in Fig. 2. Capacitance was measured with a Boonton Capacitance meter (Model 71A) operating at 1 MHz. A voltage ramp was used to apply DC bias across the film (-10 to +10 volts) at a scan speed of 0.04 volts/second. A Keithly

Model 179 digital multimeter measured current for resistivity determination, and a General Radio Model 1650-A impedance bridge was used for capacitance and resistance measurements at 1 KHz. Small signal capacitance versus applied voltage was recorded on a Hewlett-Packard 7045A X-Y recorder. Semiconductor resistance and dielectric constant measurements were carried out by evaporating aluminum contacts directly onto the semiconductor films. Dielectric constant measurements were performed at 1 MHz while resistivity measurements were carried out at both 1 KHz and under DC conditions. Ohmic contacts were always observed for the above structures. Figure 3 shows the MIS structure for Fe_2O_3 films under both positive and negative bias conditions.

RESULTS AND DISCUSSION

The results of CV and other electrical measurements for selected Fe_2O_3 and TiO_2 samples are summarized in Table 1. The dielectric constant of the iron oxide films varied from 60-113, with higher values corresponding to higher rf power levels and substrate temperatures. These values are in reasonable agreement with those reported in the literature for bulk iron oxide (80 to 120 for the α crystal form (2,12), and approximately 10 for the γ form (13)). The dielectric constant measured for the titanium dioxide film is consistent with that found for single crystal rutile (i.e., 180) along the c-axis (14). Iron oxide film resistivity varies over two orders of magnitude, depending upon deposition conditions. Similarly the resistivity of bulk iron oxide varies from 10^{-10} ohm-cm depending on processing conditions (2,15).

Relative capacitance (C/C_I) data from two Fe_2O_3 films of thickness 1.7 μm (sample 1) and 2.4 μm (sample 2) are shown in Fig. 4. Note that positive bias voltage in this plot refers to that voltage applied to the

dielectric of the MIS structure. It is clear that sample 1 shows a nearly theoretical shape as can be seen by comparison with Fig. 2. Using Eqn. [2], the carrier concentration for sample 1 is $2.6 \times 10^{16} \text{ cm}^{-3}$. On the other hand, sample 2 shows somewhat less than ideal behavior, in that a very large potential (9 volts) is required to bias the sample into accumulation. Such deviations from ideality may be due to surface states present at the semiconductor/insulator interface (16). The carrier concentration for the second sample is $3.5 \times 10^{15} \text{ cm}^{-3}$.

According to Eqn. [4], a plot of $1/C^2$ vs. bias voltage should yield a straight line. Note, however, in this case voltage is referenced to that applied to the film substrate, rather than to the aluminum contact atop the dielectric. Indeed, in agreement with Eqn. [4], both samples 1 and 2 yield a straight line on such a plot (Fig. 5), with carrier concentrations of 1.5×10^{16} and $4.9 \times 10^{15} \text{ cm}^{-3}$, respectively. These values are in reasonable agreement with results given above from application of Eqn. [2].

For comparison purposes, a number of the iron oxide samples described in Table 1 were studied using the Mott-Schottky technique. In nearly all cases, the resulting plots were non-linear, and the results were difficult to reproduce. For the sample deposited at 500°C and 50 W, a linear Mott-Schottsky plot was obtained, but the carrier concentration from this plot was $7 \times 10^{18} \text{ cm}^{-3}$, an unexpectedly high value.

As observed in Table 1, carrier concentrations for the plasma-deposited iron oxide films vary over two orders of magnitude, yet no consistent trends relating the effects of film deposition conditions to carrier concentrations are evident. Indeed, other workers have noted the difficulties of controlling the conductivity of undoped bulk polycrystalline α iron oxide materials (2).

Electron mobilities of the plasma-deposited films were calculated from the equation:

$$\mu = 1/Ne\rho \quad [5]$$

where μ is the electron mobility, and ρ is the resistivity of the film. These values are also given in Table 1. The present results are within reported values (10^{-1} to 10^{-5} $\text{cm}^2/\text{V-s}$) for bulk iron oxide (17). Titanium dioxide film mobilities are somewhat low compared to the literature value of $0.1 \text{ cm}^2/\text{V-s}$ for bulk polycrystalline material (18). However, the literature values are from samples reduced at 1450°C for two hours, thereby resulting in higher electrical conductivities than the samples in this study.

CONCLUSIONS

The Metal/Insulator/Semiconductor Capacitance-Voltage technique appears to be a useful technique for obtaining semiconductor carrier concentrations for thin film photoanodes. This technique allows the measurement of semiconductor properties independent of electrolyte. The properties of thin film SiO_2 insulators are well known and interactions between the semiconductor and the insulator are less complex and better understood than those of a liquid junction. The C-V method also displays self consistency. For example, at positive bias, the capacitance appropriate to the insulator film thickness is obtained. Moreover, the Capacitance-Voltage data can be analyzed according to Eqns. [2] and [4] in order to calculate two independent values of carrier concentration, which serve as an internal check on the experimental technique.

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Table 1. Deposition Conditions and Electrical Properties
of Thin Film Photoanodes

Power (W)	Temperature (°C)	Thickness (μm)	Electron Concentration* (cm^{-3})	Dielectric Constant	Resistivity ($\Omega\text{-cm}$)	Electron Mobility ($\frac{\text{cm}^2}{\text{V-sec}}$)
50	500	2.1	1.9×10^{16}	113	2.0×10^4	0.017
	450	2.4	4.9×10^{15}	104	4.6×10^4	.028
	400	1.9	3.8×10^{16}	94	6.5×10^3	.025
	350	1.7	1.5×10^{16}	63	1.9×10^4	.021
25	500	.51	2.6×10^{17}	60	5.7×10^3	.0042

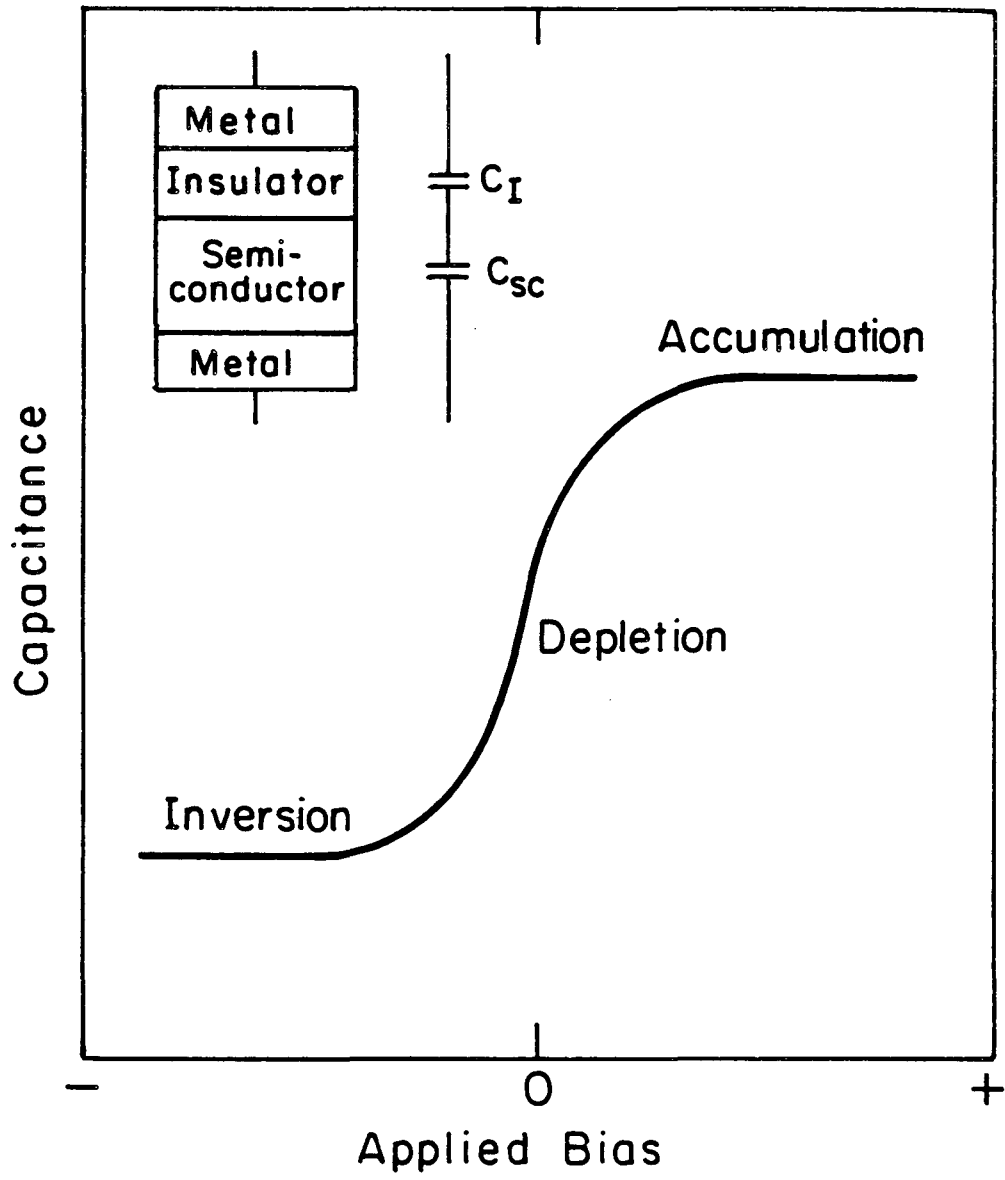
TiO_2 Films

10	430	1.2	1.0×10^{15}	160	1.1×10^6	.0055
	600	4.4	1.4×10^{15}	160	1.0×10^6	.0045

* Electron concentrations were determined from application of Eqn. [4].

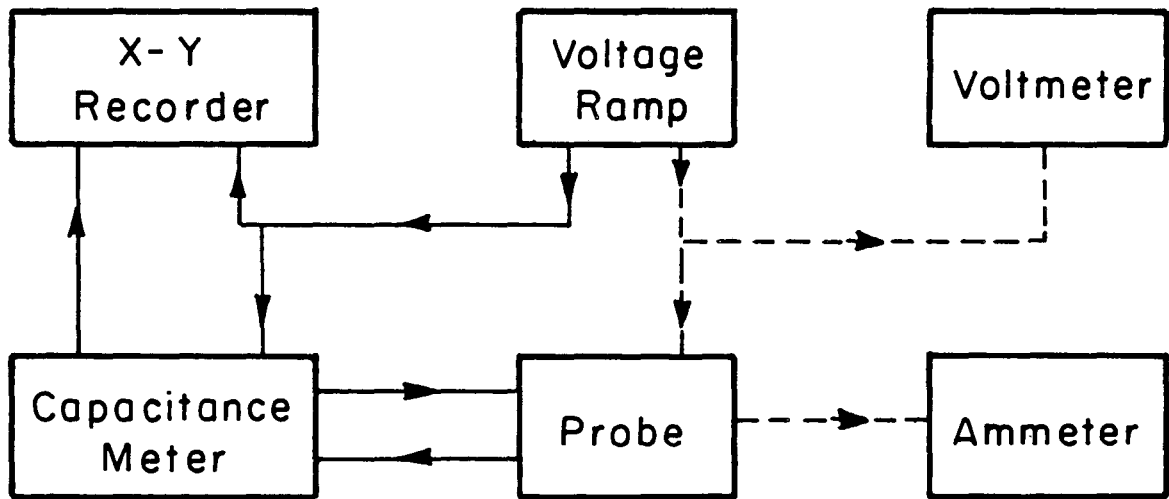
FIGURE CAPTIONS

- Fig. 1. Theoretical capacitance-voltage plot of an MIS structure. Inset at the upper left indicates the origin of the two series capacitances for this structure.
- Fig. 2. Schematic of the experimental apparatus used to measure small signal capacitance versus voltage in an MIS structure.
- Fig. 3. Schematic of the metal (Al) - insulator (SiO_2) - semiconductor (Fe_2O_3) structure used in this study. Biasing and semiconductor surface condition are indicated for depletion and accumulation regimes.
- Fig. 4. Variation of relative capacitance with DC voltage for the MIS structure shown in Fig. 3. The SiO_2 thicknesses are $0.064 \mu\text{m}$ for sample #1 ($1.7 \mu\text{m}$ Fe_2O_3) and $0.30 \mu\text{m}$ for sample #2 ($2.4 \mu\text{m}$ Fe_2O_3). See Table 1 for additional information on these samples.
- Fig. 5. Analysis of capacitance-voltage data according to Eqn. [4], for the samples of Fig. 4. The slopes of the lines are related to the carrier concentrations. Resulting values of the carrier concentration are given in Table. 1.



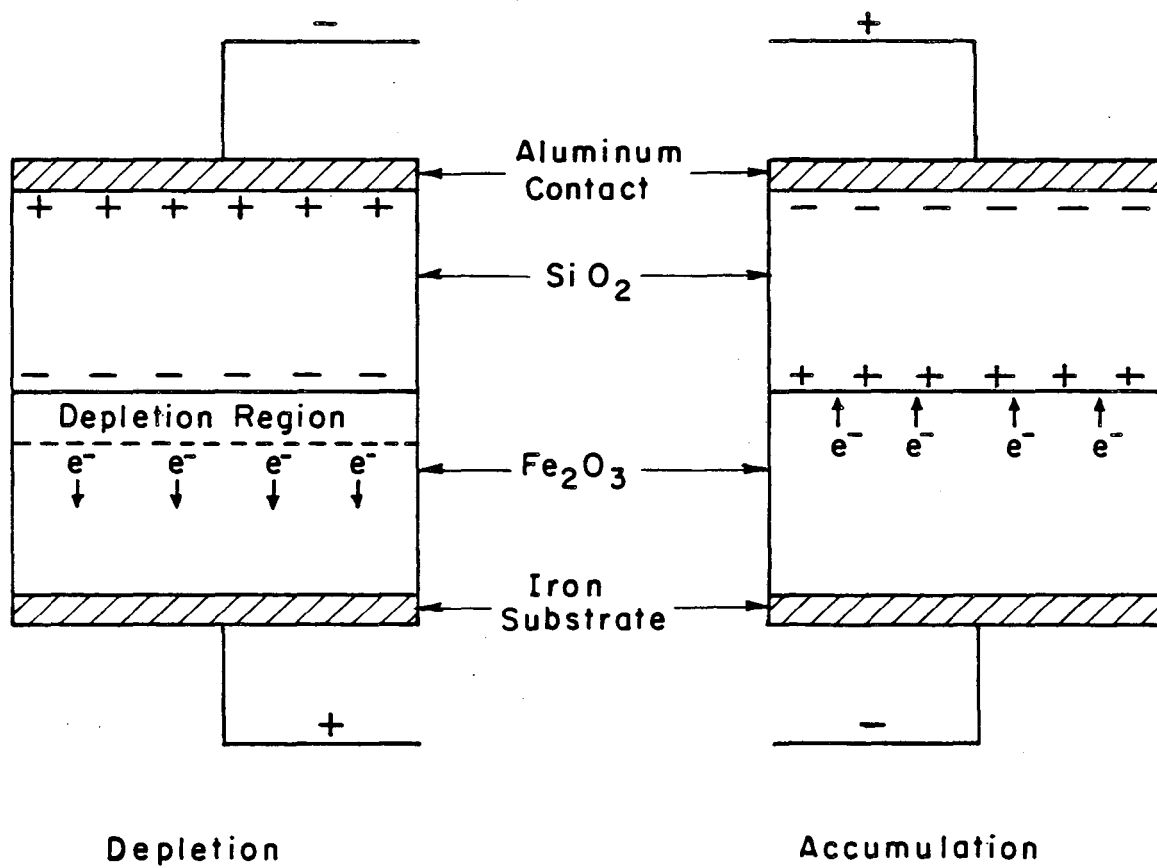
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Fig. 1



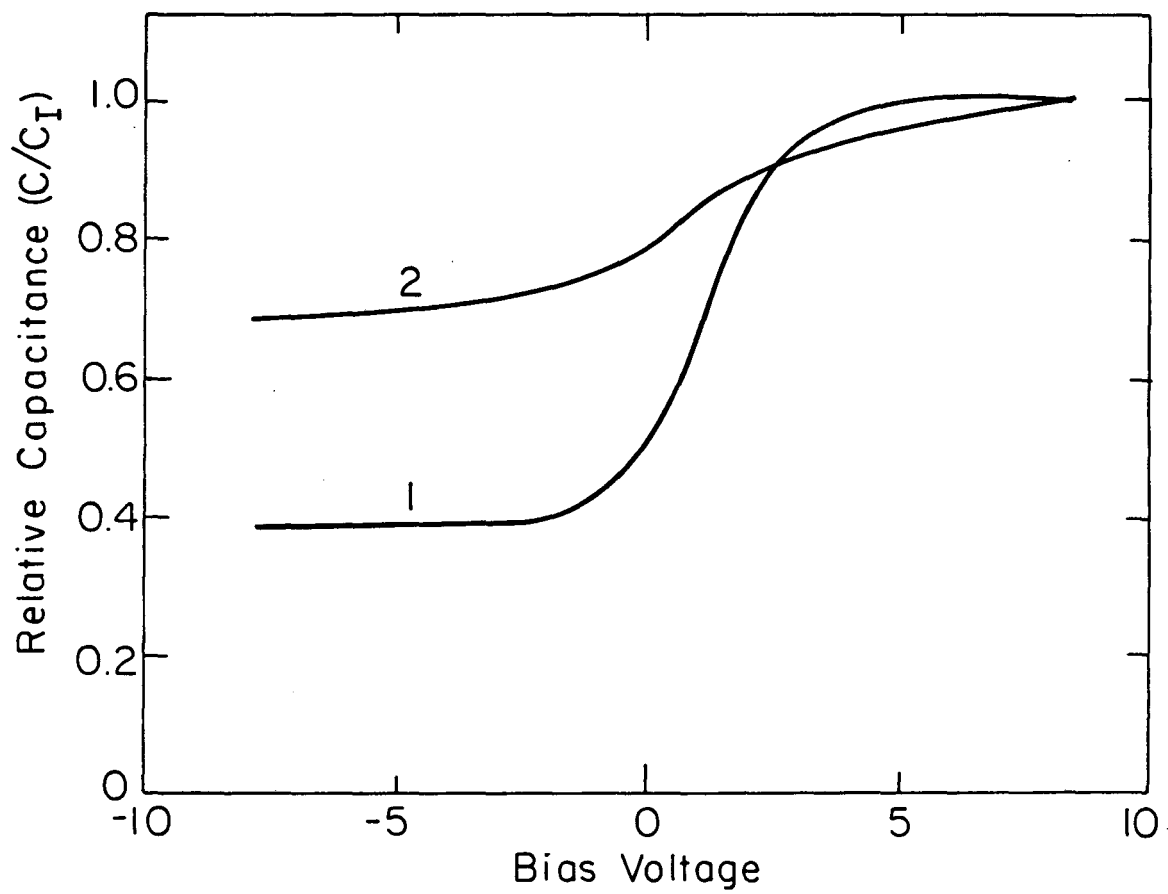
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Fig. 2



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Fig. 3



XBL 836-5842

Fig. 4

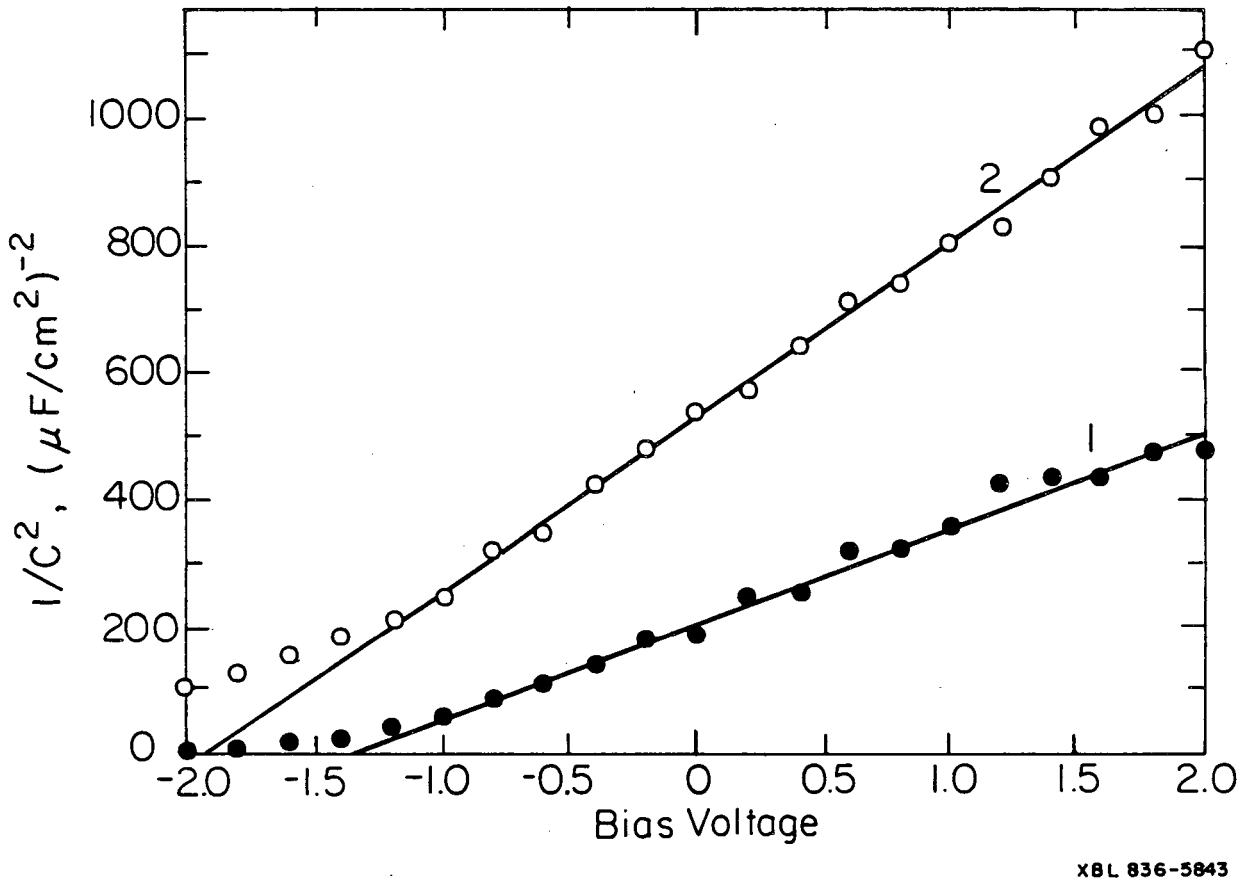


Fig. 5

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