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Progress Report

ANALYTICAL FORMULATION OF INCREMENTAL ELECTRICAL CONDUCTIVITY IN SEMICONDUCTORS ARISING FROM ACCUMULATION SPACE CHARGE LAYERS

Yin-Jang Lee

Donald R. Mason

Project Supervisor: Professor Donald R. Mason

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INTRODUCTION

In this paper, analytic expressions are derived which relate the incremental electrical conductivity in a semiconductor to the surface potential and the concentration of surface charge creating an accumulation layer.

This problem has been considered and solved by many authors,[1-4] using numerical integrations on digital computers. However, only V. B. Sandomirskii[5] has presented an approximate analytic solution to this problem. By restricting his analysis to a one-carrier semiconductor, his results are not applicable to intrinsic materials. By considering both holes and electrons in this work, additional new relationships are obtained, which satisfactorily explain several previously inexplicable experimental results.[6,7]

MODEL

The physical model assumed in this derivation is not restrictive, but is only representative. Assume that a homogeneous, relatively thin slab of non-degenerate semiconductor material is oriented as shown in Figure 4.1 with electrical contacts being made uniformly on the x-z planes at the ends of the bar which are perpendicular to the y-axis. The extent of the bar in the y-direction is not important, and the electric field is applied in the y-direction. Furthermore

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The Department of Chemical and Metallurgical Engineering
The University of Michigan
Ann Arbor, Michigan

ABSTRACT

An analytic expression is derived which relates the incremental electrical conductivity in an accumulation layer on a semiconductor to the concentration of surface ions. The theory is checked both by comparing the predicted results with published graphs which were obtained by numerical integrations, and by evaluating three separate sets of experimental data, two of which seem to be within the limitations of this theory.

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(1) The height, W, of the semiconductor slab is assumed to be much larger than the half width, L, which in turn is large in comparison with the thickness of the space charge region, δ. That is, $W \gg L \gg \delta$. Therefore, the surface charge on the x-y planes at $z = 0$ and $z = W$ can be neglected.

(2) The electron mobility μ_n and hole mobility μ_p are assumed to be constant throughout the space charge region and equal to the corresponding carrier mobilities in the bulk. This can be regarded as a zero order approximation.

We shall now proceed to the formulation of the incremental electrical conductivity, $\Delta\sigma_s$ associated with one face of a p-type semiconductor slab as a function of surface charge concentration arising from ionized acceptors, $[A^-]$, on that face, expressed as charged centers/cm.^{2} The microscopic current density, j(x), is given as

$$j(x) = q\left[n(x)\mu_n + p(x)\mu_p\right]\mathcal{E} \qquad (4.1)$$

The carrier concentrations are related to the surface potential by the relationships

$$u(x) = Y(x)/kT$$

where Boltzmann statistics are used in the relationships

$$n(x) = n_B \exp u(x);\; p(x) = p_B \exp -u(x) \qquad (4.2)$$

For a negative surface charge, $[A^-]$, then $u(x) = -u'(x)$ where $u'(x)$ is always positive or zero. For a positive surface charge, $[D^+]$, then u(x) may be negative. In the interior of the semiconductor, over the half-width of the bar.

$$j(o) = q\left[n_B\mu_n + p_B\mu_p\right]\mathcal{E} = I_o/WL \qquad (4.3)$$

The incremental current density due to the diffusion potential then can be defined as the difference between Equations (4. 1) and (4. 3). That is

$$\Delta j(x) = j(x) - j(0) = q\left\{\mu_n n_B \left[\exp(-u') - 1\right] + \mu_p p_B \left[\exp(u') - 1\right]\right\}\mathcal{E} \quad (4.4)$$

By defining integral incremental carrier concentrations, Garrett and Brattain,[1] Kingston and Neustadter,[2] Greene,[3] and Mowery[4] have also defined Equation (4. 4) and the latter three authors have integrated the equation by numerical methods.

Mathematical Formulation

The general problem can be delineated more clearly by referring to Figure 4. 2, adapted from Buck and McKim[8] for p-type silicon. As surface acceptors are added, an accumulation layer is formed and the incremental surface conductivity increases. As surface donors are added, a depletion layer is formed producing a decrease in $\Delta\sigma_S$ to some minimum value corresponding approximately to the formation of an intrinsic surface. (The minimum is shifted by differences in the electron and hole mobilities.) As an inversion layer is formed the conductivity starts to increase, but $\Delta\sigma_S$ does not become positive until the gain in conductivity from the inverted region of the surface layer compensates for the loss of conductivity arising from the depleted region of the surface layer. This compensation would be expected to occur when the inverted surface potential is approximately twice the bulk diffusion potential. When the surface is more highly inverted then $\Delta\sigma_S$ becomes positive and appears to be similar to an accumulation layer. To a good approximation, a highly inverted layer can be approximated as an accumulation layer.

For accumulation layers the diffusion potential can be considered to increase smoothly from zero in the interior to some value u'_s on the surface of the semiconductor. For a highly inverted layer, the conductivity can be assumed to be dominated by the inverted region beyond the mirrored bulk diffusion potential, u_B, so that the limits of integration for the diffusion potential would extend from $2\,u_B$ to u_s or more simply from zero to $(u_s - 2\,u_B)$. In the remaining derivations, the accumulation is considered but the extension to the highly inverted layer can be readily made as indicated.

The following transformation can be made in Equation(4.4).

$$\Delta j(x) = q\mathcal{E}(\mu_n n_B \mu_p p_B)^{1/2}\left\{\left(\frac{\mu_n n_B}{\mu_p p_B}\right)^{1/2}\left[\exp(-u') - 1\right] + \left(\frac{\mu_p p_B}{\mu_n n_B}\right)^{1/2}\left[\exp(u') - 1\right]\right\} \quad (4.5)$$

For negative surface charge (i.e., acceptors) on a p-type semiconductor let

$$\theta = \ln(\mu_p\, p_B/\mu_n\, n_B)^{1/2} \quad (4.6)$$

Then

$$\exp\theta = (\mu_p\, p_B/\mu_n\, n_B)^{1/2};\exp(-\theta) = (\mu_n\, n_B/\mu_p\, p_B)^{1/2} \quad (4.6a)$$

Now define an artificial conductivity, σ_{Avg}, as

$$\sigma_{Avg} = q\, n_i\, (\mu_n\, \mu_p)^{1/2} \quad (4.7)$$

and combine Equations (4.6a), (4.7) and (4.5) to give

$$\Delta j(x) = \sigma_{Avg}\mathcal{E}\left\{\exp\left[-(\theta+u')\right] - \exp\left[-\theta\right] + \exp\left[\theta+u'\right] - \exp\left[\theta\right]\right\}$$

which also can be written as

$$\Delta j(x) = 2\mathcal{E}\sigma_{Avg}\left[\cosh(\theta + u') - \cosh\theta\right] \quad (4.8)$$

The total increment of current is the integral of the incremental current density over the half-width of the slab. That is

$$\Delta I = 2 W \mathcal{E} \sigma_{Avg} \int_0^L \left[\cosh(\theta + u') - \cosh\theta\right] dx \qquad (4.9)$$

The variable of integration in Equation (4.9) can be changed from x to u' since

$$dx = du'/(du'/dx) \qquad (4.10)$$

Lee and Mason[9] showed that for accumulation layers and for highly inverted layers, the following approximation is valid.

$$\frac{du'}{dx} \cong -4 (L_m p_B)^{1/2} \sinh(u'/2) \qquad (4.11)$$

Since the origin has been changed in this work from the surface of the semiconductor to a point inside the semiconductor, then it is necessary to change the negative sign in Equation (4.11) to a positive sign. Therefore

$$\frac{du'}{dx} \cong +4 (L_m p_B)^{1/2} \sinh(u'/2) \qquad (4.12)$$

Equation (4.12) is an exact expression for an intrinsic semiconductor, and is a first order approximation for acceptors on a p-type semiconductor (or for donors on an n-type semiconductor with a positively charged surface).

Combine Equations (4.10) and (4.12).

$$dx = \frac{du'}{4 (L_m p_B)^{1/2} \sinh(u'/2)} \qquad (4.13)$$

Substitution of Equation (4.13) into Equation (4.9) then gives

$$\Delta I \cong \frac{2 W \mathcal{E} \sigma_{Avg}}{4 (L_m p_B)^{1/2}} \int_0^{u'_s} \frac{\left[\cosh(\theta + u') - \cosh\theta\right] du'}{\sinh(u'/2)} \qquad (4.14)$$

where the appropriate new boundary conditions have been substituted.

$$\text{from } x = 0 \qquad \text{to } u' = 0, \tag{4.15}$$

and

$$\text{from } x = L \qquad \text{to } u' = u'_s \tag{4.16}$$

The following hyperbolic trigonometric identities can be used to simplify the integral in Equation (4.14).

$$\cosh(\theta + u') = \cosh\theta \left[1 + 2\sinh^2\left(\frac{u'}{2}\right)\right] + 2\sinh\theta\sinh\left(\frac{u'}{2}\right)\cosh\left(\frac{u'}{2}\right)$$

$$\frac{\cosh(\theta+u') - \cosh\theta}{\sinh\left(\frac{u'}{2}\right)} = 2\cosh\theta\sinh\left(\frac{u'}{2}\right) + 2\sinh\theta\cosh\left(\frac{u'}{2}\right) = 2\sinh\left(\theta+\frac{u'}{2}\right) \tag{4.17}$$

Combine Equations (4.17) and (4.14).

$$\Delta I \cong \frac{4 W\mathcal{E}\sigma_{Avg}}{4 (L_m p_B)^{1/2}} \int_0^{u'_s} \sinh\left(\theta+\frac{u'}{2}\right) du' = \frac{8 W\mathcal{E}\sigma_{Avg}}{4 (L_m p_B)^{1/2}} \int_0^{u'_s/2} \sinh(\theta+u'/2)\, d(\theta+u'/2)$$

Therefore, performing the integration

$$\Delta I = \frac{2 W\mathcal{E}\sigma_{Avg}}{(L_m p_B)^{1/2}} \left\{\cosh(\theta + u'_s/2) - \cosh(\theta)\right\} \tag{4.18}$$

Note that when $u'_s = 0$, then $\Delta I = 0$, which is required on the basis of the physical conditions expressed by Equations (4.14) and (4.16). Furthermore since

$$\cosh(\theta + u'_s/2) = \cosh\theta\left[1 + 2\sinh^2(u'_s/4)\right] + \sinh\theta\sinh(u'_s/2)$$

then Equation (4.18) can be written

$$\Delta I = \frac{2 W\mathcal{E}\sigma_{Avg}}{(L_m p_B)^{1/2}} \left\{2\cosh\theta\sinh^2(u'_s/4) + \sinh\theta\sinh(u'_s/2)\right\} \tag{4.19}$$

The incremental surface conductivity, $\Delta\sigma_s$, can be defined from Equation (4.19) as

$$\Delta \sigma_s = \frac{\Delta I}{W\mathcal{E}} = \frac{2\,\sigma_{Avg}}{(L_m p_B)^{1/2}} \left\{ 2 \cosh \theta \sinh^2 (u'_s/4) + \sinh \theta \sinh (u'_s/2) \right\} \qquad (4.20)$$

This is also equivalent to the incremental sheet conductivity which is often used in semiconductor surface work, and has the units of mhos per "square."

These equations relate the excess current and the incremental surface conductivity of the accumulation layer on the surface of the semiconductor to the surface potential, the bulk properties and the geometry of the sample. This equation now can be extended to define the incremental electrical conductivity in terms of the surface charge concentration. Simple relationships can be obtained for high surface coverage and low surface coverage, but a much more complicated relationship defining the general case must be used for intermediate surface coverages.

High Surface Coverage ($u'_s \geq 8$).

For high surface coverage, when $u'_s \geq 8$, then $\sinh(u'_s/4) \simeq \cosh(u'_s/4)$ within 4%. Equation (4.20) can be written as

$$\Delta \sigma_s = \frac{2\,\sigma_{Avg}}{(L_m p_B)^{1/2}} \left\{ (\cosh \theta + \sinh \theta) \sinh (u'_s/2) \right\} \qquad (4.21)$$

Lee and Mason[9] have also shown that in general the surface potential can be related to the surface ion concentration by the relationship

$$\sinh (u'_s/2) = (L_m/p_B)^{1/2} \left[A^-\right]/2 \qquad (4.22)$$

Another simplification can be made in Equation (4.21) simultaneously by using the definitions from Equations (4.6) and (**4.**7).

$$2\sigma_{Avg} \cosh\theta = q(\mu_n n_B + \mu_p p_B)$$

$$2\sigma_{Avg} \sinh\theta = q(\mu_p p_B - \mu_n n_B)$$

Substitution gives

$$\Delta\sigma_s = q\mu_p \left[A^-\right] \qquad (4.23)$$

The incremental surface conductivity then is proportional to the hole (majority carrier) mobility and the surface ion concentration.

This relationship now can be used to define the fractional change in current or the fractional change in total conductivity for a particular sample arrangement or a particular experimental system. Using the model defined in Figure 4.1 it follows directly that

$$\frac{\Delta I}{I_o} = \frac{I - I_o}{I_o} = \frac{(\sigma - \sigma_o)\ WL}{\sigma_o\ WL} = \frac{\Delta\sigma}{\sigma_o} \qquad (4.24)$$

where

$$\sigma_o = q(\mu_n n_B + \mu_p p_B)$$

The relationship between $\Delta\sigma$ and $\Delta\sigma_s$ can be obtained from Equations (4.20) and (4.24).

$$\Delta\sigma_s = \frac{\Delta I}{W} = \frac{\Delta\sigma\ W\ L}{W} = \Delta\sigma\ L \qquad (4.25)$$

Substitution of Equation (4.23) and (4.25) into (4.24) then gives

$$\frac{\Delta I}{I_o} = \frac{\Delta\sigma}{\sigma_o} = \frac{\mu_p \left[A^-\right]}{L(\mu_n n_B + \mu_p p_B)} \qquad (4.26)$$

For semiconductors wherein the electron contribution to the total conductivity is negligible then Equation (4.26) becomes

$$\frac{\Delta I}{I_o} = \frac{\Delta \sigma}{\sigma_o} = [A^-]/ L p_B \qquad (4.27)$$

This latter expression has also been derived by Sandomirskii.[5]

<u>Low Surface Coverage ($u'_s \lesssim 1$).</u>

For low surface coverage, when $u'_s \lesssim 1$, then

$$\sinh (u'_s/2) \simeq (u'_s/2) \text{ within } 4\%.$$

Similarly

$$(\sinh u'_s/4)^2 = (u'_s/4)^2 = u'^2_s/16 = (L_m/p_B) [A^-]^2/16$$

Substitution of these relationships and those used in the preceding section into Equation (4.20) gives the incremental surface conductivity as

$$\Delta \sigma_s = \frac{q}{2 p_B}\left\{\frac{(\mu_p p_B + \mu_n n_B)(L_m/p_B)^{1/2}}{4} [A^-]^2 + (\mu_p p_B - \mu_n n_B) [A^-]\right\} \qquad (4.28)$$

The fractional change in total conductivity is

$$\frac{\Delta I_o}{I_o} = \frac{\Delta \sigma}{\sigma_o} = \frac{1}{2 L p_B}\left\{\frac{(L_m/p_B)^{1/2}}{4} [A^-]^2 + \left(\frac{\mu_p p_B - \mu_n n_B}{\mu_p p_B + \mu_n n_B}\right) [A^-]\right\} \qquad (4.29)$$

This expression is significantly different from that derived by Sandomirskii,[5] in that his expression contains no quadratic dependency of the excess conductivity on surface ion concentration. This quadratic dependency would be most apparent on intrinsic or lightly doped semiconductors.

Generalized Relationship (Required when $1 < u'_s < 8$).

When the surface potential is neither large nor small, the simplifying approximations used in the preceding sections are not applicable. However, the following hyperbolic identity

$$2 \sinh^2 (u'_s/4) = \left[1 + \sinh^2 (u'_s/2)\right]^{1/2} - 1$$

can be substituted into Equation (4.20), followed by the same relationships already used above to give

$$\Delta\sigma_s = \frac{q(\mu_p p_B + \mu_n n_B)}{(L_m p_B)^{1/2}} \left\{ \left[1 + (L_m/p_B) \left[A^-\right]^2/4\right]^{1/2} - 1 + \frac{(L_m/p_B)^{1/2} (\mu_p p_B - \mu_n n_B)}{2(\mu_p p_B + \mu_n n_B)} \left[A^-\right] \right\} \tag{4.30}$$

The fractional change in total conductivity then becomes

$$\frac{\Delta I}{I_o} = \frac{\Delta\sigma}{\sigma_o} = \frac{1}{L(L_m p_B)^{1/2}} \left\{ \left[1 + (L_m/p_B) \left[A^-\right]^2/4\right]^{1/2} - 1 + \frac{(L_m/p_B)^{1/2} (\mu_p p_B - \mu_n n_B)}{2(\mu_p p_B + \mu_n n_B)} \left[A^-\right] \right\} \tag{4.31}$$

For the case of low surface coverage this equation reduces readily to Equation (4.29).

The above formulations are for an intrinsic or p-type semiconductor with a negative surface charge. The results for an intrinsic or n-type semiconductor with positive surface charge are similar and can be easily written down by analogy.

From the foregoing analysis it is apparent that two types of tests can be made. First, the results obtained from the analytical mathematical solutions can be compared with results obtained by numerical integration methods. Second, the derived equations can be checked against experimental data.

Numerical Evaluation

By using numerical integration techniques, Mowery[4] has presented

graphs relating incremental surface conductivity, $\Delta\sigma_s$, (which he calls ΔG), to the electrical conductivity and surface potential for germanium and silicon. This same relationship for accumulation layers is represented by Equation (4.20) above. Mowery has also presented a graphical correlation between surface charge and surface potential for germanium and silicon. This is expressed in general form for accumulation layers on any semiconductor by Equation (4.22) above.

By inserting the appropriate numbers used by Mowery into the equations derived above, the results given on his graphical correlations have been obtained within the ability to read the published graphs. This then constitutes a satisfactory check on the mathematical operation.

Inversely, a measurement of $\Delta\sigma_s$ now can be used to ascertain the surface ion concentration. In Figure 4.3, Equation (4.30) is plotted, showing $\Delta\sigma_s$ as a function of ionized surface acceptor concentration $[A^-]$ on intrinsic and 1 ohm-cm p-type germanium. Similar curves are also shown for ionized surface donor concentration $[D^+]$ on intrinsic and 1 ohm-cm n-type germanium. The minimum in the curve for ionized acceptors on intrinsic germanium arises from the coefficient of the linear term, which is negative because the hole mobility is lower than the electron mobility. However, when donor ions are placed on germanium, there is no minimum in the $\Delta\sigma_s$ vs $[D^+]$ curve, as shown on Figure 4.3.

Experimental Evaluation

Three sets of experimental data are available[6, 7, 13] which may be used to ascertain the validity of the theories presented above. Although none of these works give a good quantitative check of the theories in all aspects, the observed trends are semi-quantitatively

correct. Each set of data is discussed separately.

Weller and Voltz[6] have published data showing changes in electrical conductivity of sintered Cr_2O_3 as a function of the concentration of oxygen adsorbed on the surface. Their data is plotted in Figure 4.4, showing $\Delta\sigma/\sigma_o$ as a function of net O_2 adsorbed in micromoles/gm. In another publication,[10] they reported that the surface area of this material was equal to 35 meter^2/gm. Using the measured density of 5.1 (by water immersion) and assuming a smooth surface, they computed the average particle diameter to be 335 Å. This particle size would increase linearly as a function of surface roughness, and since a roughness factor of from 5 to 10 is reasonable, the particle size probably is in the range of 0.1 to 0.3 microns.

By making an approximate computation using an as yet unpublished adsorption theory,[12] and assuming a shallow surface acceptor level, then it appears that most of the oxygen atoms on the surface are ionized. The correlation in Figure 4.4 shows that

$$(\Delta\sigma/\sigma_o) = 4.4 \times 10^{-15} \, [0] \tag{4.32}$$

where

$\Delta\sigma/\sigma_o$ = fractional conductivity change

$[0]$ = oxygen atoms adsorbed/cm.^{2}

A comparison of this result with Equation (4.27) shows that

$$p_B = \frac{10^{15}}{4.4L} \frac{[0^-]}{[0]} \approx 10^{19} \text{ holes/cm}^3 \tag{4.33}$$

where a shape factor in the numerator determined from the particle geometry and the surface-to-volume ratio has been assumed as unity. This is not unreasonable in view of other assumptions used in the computation.

Weller and Voltz also report an original "conductivity," σ_o, in the absence of adsorbed oxygen, as 1.4×10^{-4} ohm-cm. This presumably

is for the particulate solid, and should be somewhat greater for a homogeneous solid. However, using this value of σ_o with the hole concentration obtained above, it follows that the hole mobility $u_p \simeq 10^{-3}$ cm^2/volt sec at 500^oC. This then represents a minimum value, and an actual value 10 or 100 times greater is not unreasonable. Independent mobility measurements do not seem to have been made on this material. However, Chapman, Griffith and Marsh[11] reported Hall and conductivity measurements on 70% Cr_2O_3 - 30% Al_2O_3 which is an n-type semiconductor. In this material the free electron concentration was 3.5×10^{13} electrons/cm.^{3} and the Hall mobility was 2 cm^2/volt sec at 442^oC. Therefore, it appears that the hole mobility obtained in this work may be somewhat low, but nevertheless is in the right order of magnitude.

Chapman, et. al. have also shown that from 400^oC to 500^oC, the effective energy gap of Cr_2O_3 annealed in oxygen is 1.22 eV. This apparently represents a deep acceptor level since gap values of 2.50 eV and 2.86 eV were obtained on materials annealed in hydrogen and vacuum, respectively.

By assuming that the concentration of acceptor levels is $3 \times 10^{20}/cm^3$ (from 75 μ moles excess O_2/gm, and 1.5 excess O atoms create one Cr vacancy, which creates one acceptor level), that holes are created by ionizing these acceptors, and that the concentration of states in the valence band is equal to $4.83 \times 10^{15}\ T^{3/2} \simeq 10^{20}$, then it follows that the Fermi level is at $E_a/2$, and $p_B \simeq 10^{16}$ holes/cm^3. The agreement with the previously ascertained value of 10^{19} holes/cm^3 is poor. For $\Delta\sigma/\sigma_o = 0.1$, then the surface potential computed from $p_B = 10^{19}$ and $L_m = 10^{-6}$ gives $u'_s \simeq 3.8$, which is marginally low.

It is apparent then that these data do not completely check the theory, although qualitative trends are followed. The discrepancies may be ascribed to the small particle size of this material, since it is not large when compared with the computed screening length ($L_s = 1/2\ (L_m\ p_B)^{1/2} = 5 \times 10^{-6}$cm).

A. W. Smith[13] has published data showing changes in conductivity in thin films of CuO as a function of oxygen adsorbed on the surface. However, from the rather subjective manner in which the paper is written, it is difficult to ascertain exactly what the author has done experimentally, and his theorical section contains errors. A careful reading of the manuscript seems to support the conclusions that his fully covered surface (not achieved) would contain about 2×10^{14} oxygen atoms/cm^2, that his reference conductance (g_o) for film 3 is 44 μ mho for the conditions reported in Smith's Figure 4, that the film thickness of film 3 is 0.1 micron, and that the reported measurements of conductance as a function of surface coverage were made at 127°C (not critical). Smith's data are plotted in Figure 5, showing $\Delta\sigma/\sigma_o$ as a function of adsorbed oxygen concentration, $[0]$.

Smith observes that some oxygen is adsorbed immediately which has no influence on the film conductance. These atoms presumably form a surface dipole layer, or fill covalent surface states, but do not ionize nor form a space charge region. Above 1.8×10^{13} oxygen atoms/cm^2 but below 6×10^{13} oxygen atoms/cm^2 the fractional conductivity increases linearly with adsorbed oxygen concentration. From the slope of this curve, it follows that $p_B = 5 \times 10^{17}$ holes/cm^3. Smith indicates that the conversion from conductance to conductivity in his system of units requires a factor of 4×10^3. Therefore $\sigma_o = 0.176$ mho/cm, from which it follows from p_B above that the hole mobility $\mu_p \simeq 2$ cm^2/volt sec. This is a reasonable value, since it is a factor of 10 less than that for Cu_2O.[14]

By assuming that the dielectric constant of CuO is 10, then $L_m = 3 \times 10^{-6}$ cm, the screening length, $L_s = 1/2 \sqrt{L_m p_B} = 4 \times 10^{-7}$ cm so that the film thickness is equal to about 25 L_s.

When the incremental conductivity has increased 3.5 times, the net surface ion concentration contributing to the space charge is 2×10^{13} oxygen atoms/cm^2 and the surface potential $u'_s = 7.8$. It appears therefore that these data confirm the assumptions made in this theory for moderate surface coverages.

Molinari, et. al.[7] have measured changes in the electrical conductivity of compressed beds of Zn O powder as a function of surface treatment, hydrogen gas pressure, time, and temperature. Again, important experimental details are omitted from their paper, but it appears that the relationship between these data and our theory is that

$$\Delta\sigma_{s,1} - \Delta\sigma_{s,0} = \frac{\Delta\chi hd}{4S} \qquad (4.34)$$

where

$\Delta\sigma_{s,1}$ = final surface conductance, mho/square

$\Delta\sigma_{s,0}$ = reference surface conductance, mho/square

$\Delta\chi$ = reported conductance change, mho

h = distance between platinum contacts, cm

d = average particle dimension, cm

S = area of platinum contacts, cm^2.

We shall assume then that h/S is approximately unity, that $\Delta\sigma_{s,0}$ is zero or small relative to $\Delta\sigma_{s,1}$, and that the average particle dimension is given by $d = 6f/\rho A$, where f = roughness factor, ρ = density, and A = surface area, cm^2/gm. For a surface roughness factor of 2, then $d \simeq 4 \times 10^{-4}$ cm. These authors also find an initial large adsorption after surface cleaning which occurs so rapidly that its influence on surface conductivity cannot be followed. This initial uptake is a function of temperature and gas pressure. The changes discussed here are those occurring after the reference conditions have been established as a result of initial gas uptake.

For Zn O heat treated in vacuum, the reference conductance χ_o was measured as a function of temperature. At 57^oC, $\chi_o \simeq 10^{-5}$ mho. After subtracting out the initial amount of hydrogen adsorbed at various

pressures, their data at 57°C showing $\Delta\chi/\chi_o$ vs net adsorbed hydrogen concentration are given in Figure 4.6. From the high coverage theory given in Equation (4.27) and adapted to n-type material it follows that

$$\frac{\Delta\chi}{\chi_o} = \frac{\Delta\sigma}{\sigma_o} = \frac{[H]}{L\, n_B} \frac{[H^+]}{[H]} \qquad (4.35)$$

Since $L \simeq d/2$, then

$$\frac{n_B}{[H^+]/[H]} = \frac{2\,[H]\,\chi_o}{d\,\Delta\chi} = 2.3 \times 10^{16} \qquad (4.36)$$

Since a reasonable carrier concentration for ZnO is about 10^{17} carriers/cm^3, it appears that most of the hydrogen atoms are ionized. When these data are considered in conjunction with adapted forms of Equations (4.23) and (4.34), then

$$\Delta\sigma_s = \frac{\Delta\chi\, h\, d}{S} = q\,\mu_n\,[H]\,([H^+]/[H]) \qquad (4.37)$$

or

$$\mu_n = \frac{\Delta\chi\, d}{q\,[H]\,([H^+]/[H])} = 5.4 \times 10^{-3}\ \text{cm}^2/\text{volt sec} \qquad (4.38)$$

By also computing μ_n from the bulk conductivity relationship for an n-type semiconductor

$$\chi_o = \frac{\sigma_o S}{h} = \frac{S}{h}(n_B\, q\, \mu_n) = 10^{-5}\ \text{mho} \qquad (4.39)$$

Using the assumptions and conclusions above it is found that $\mu_n \simeq 2.7 \times 10^{-3}$ cm^2/volt sec. which agrees within a factor of 2 of the value found from the incremental conductivity theory above. This can be compared with a value of about 100 cm^2/volt sec for single crystals of

ZnO, so that this indicates a large decrease in mobility in the compressed particles form of the material.

CONCLUSIONS

An analytic expression has been derived which relates the incremental electrical conductivity in an accumulation layer on a semi-conductor to the concentration of surface ions. The theory has been checked against published graphs which were obtained by numerical integrations. Three separate sets of experimental data were also used to check the theory. The data of Weller and Voltz[6] for the effect of oxygen adsorbed on Cr_2O_3 does not fit the assumptions of the theory, since their particles are too small. The data of Smith[7] for oxygen adsorbed on CuO, and the data of Molinari et. al.[13] for hydrogen on ZnO indicate that the observed trends are all in the proper direction and of the proper magnitude to support this work, but they are not of sufficient precision to support these derivations conclusively. Although definitive quantitative experimental check remains to be done, the reasonableness of the derivation has been established.

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Figure Captions

Fig. 4.1. Slab of semiconductor of height W and width 2L, with electrical contacts on x-z planes and electric field $\mathcal{E}$ in the y-direction.

Fig. 4.2. Incremental surface conductivity as function of surface potential on 140 ohm-cm p-type silicon.

Fig. 4.3. Computed relationships between $\Delta\sigma_s$ and surface ion concentrations on germanium at 300°K.

Fig. 4.4. Normalized incremental electrical conductivity increase of sintered Cr_2O_3 as function of amount of adsorbed oxygen.

Fig. 4.5. Normalized incremental electrical conductivuty of a CuO film as a function of surface oxygen concentration.

Fig. 4.6. Normalized incremental electrical conductivity of compressed ZnO powder as a function of surface oxygen concentration.

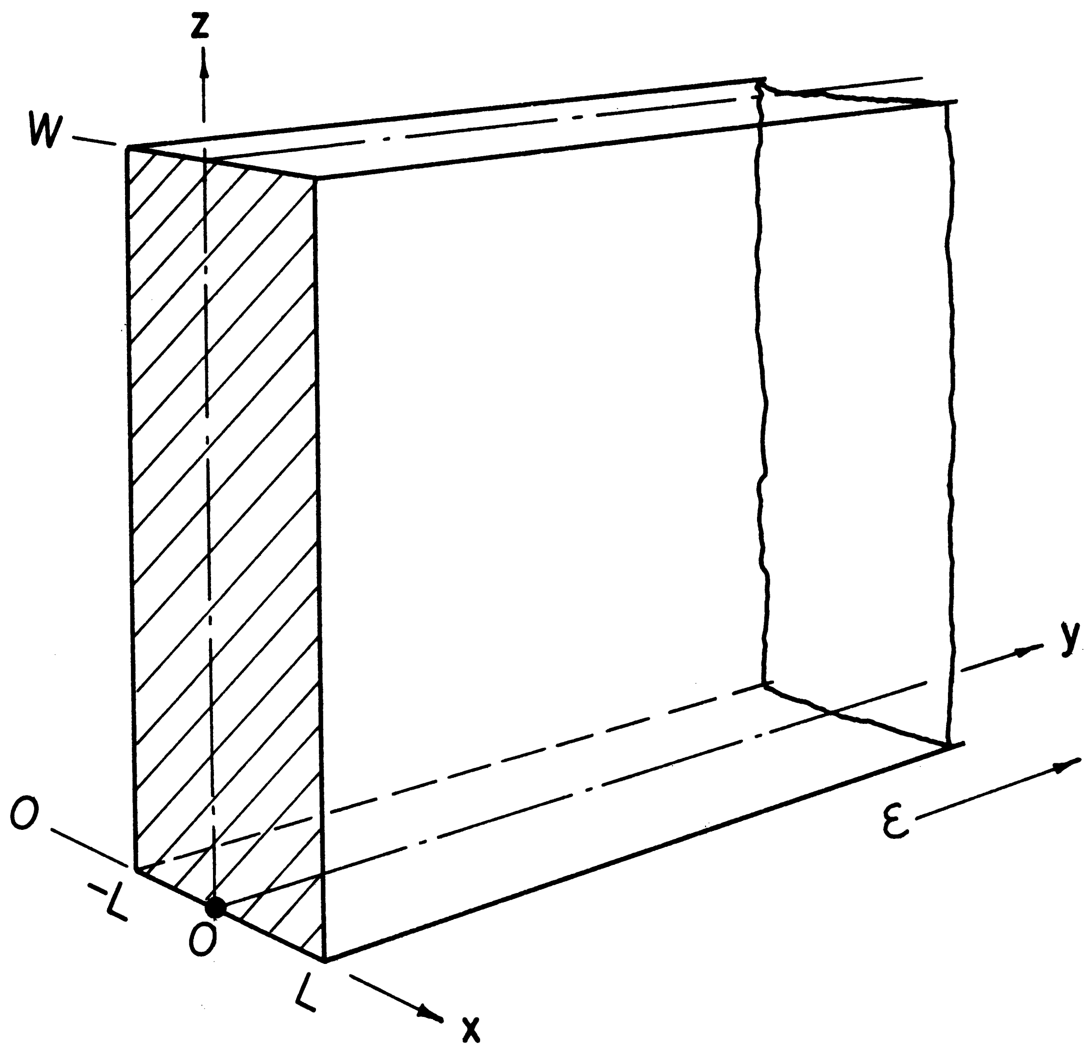

Fig. 4.1.

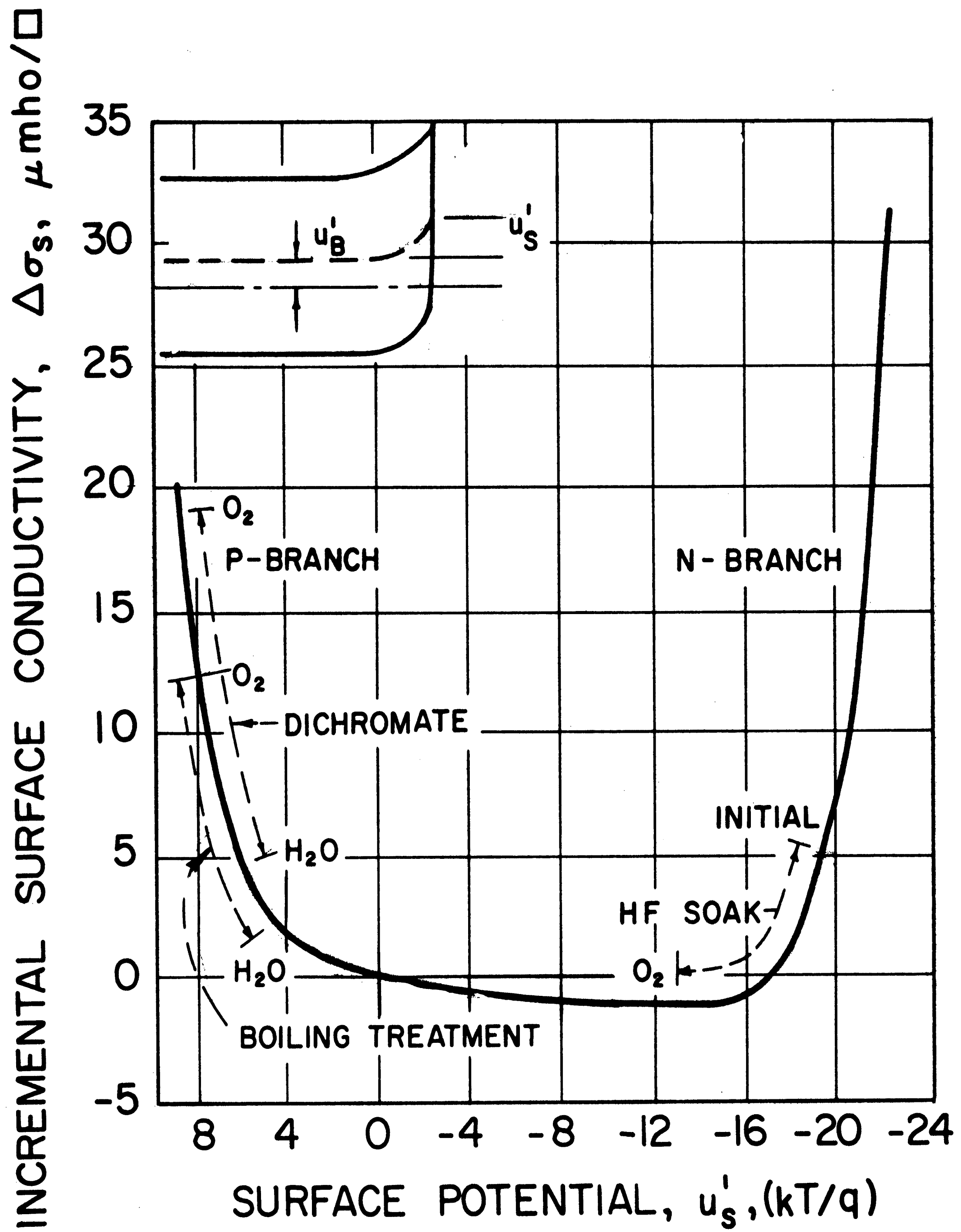

Fig. 4.2.

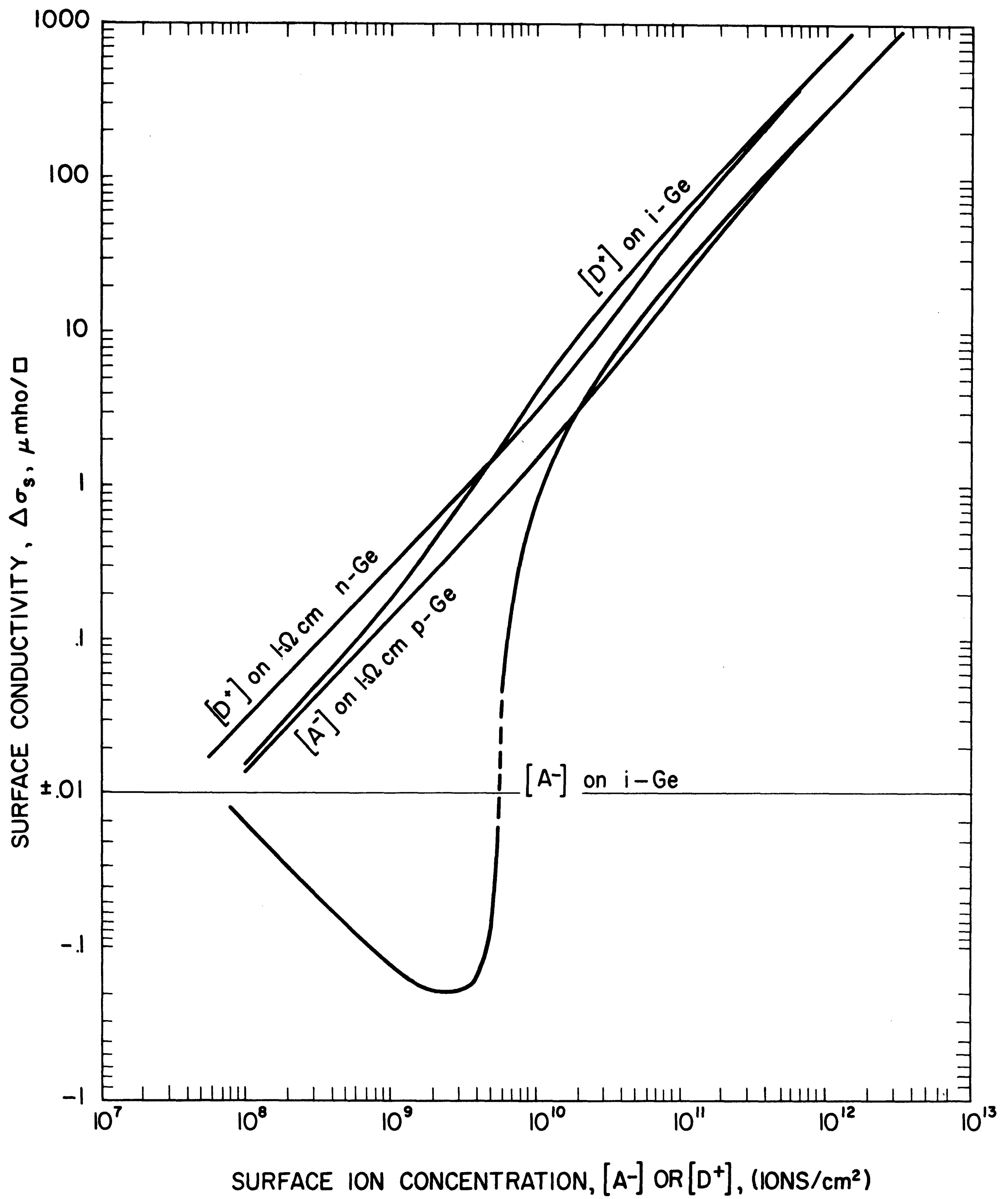

Fig. 4.3.

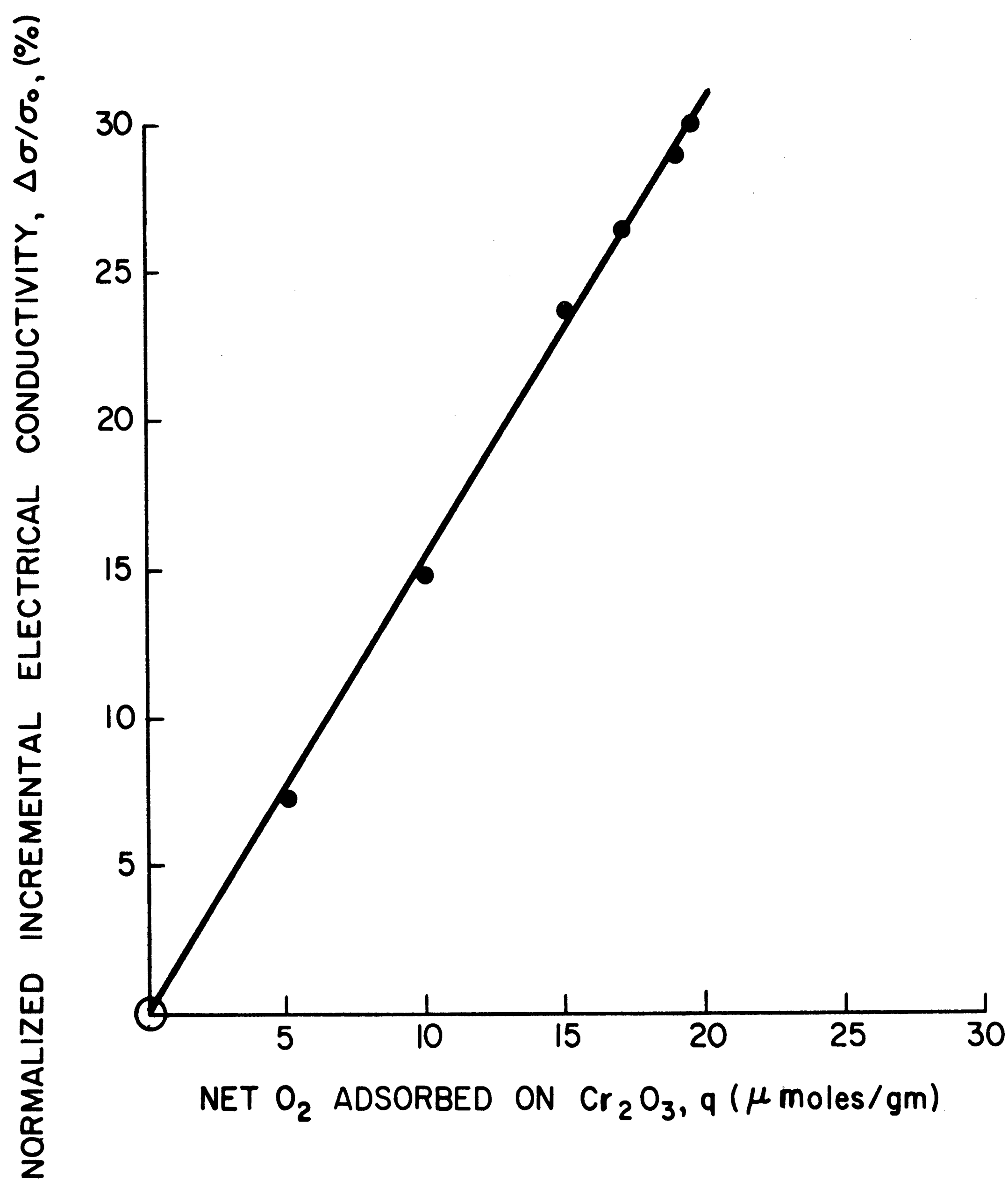

Fig. 4.4.

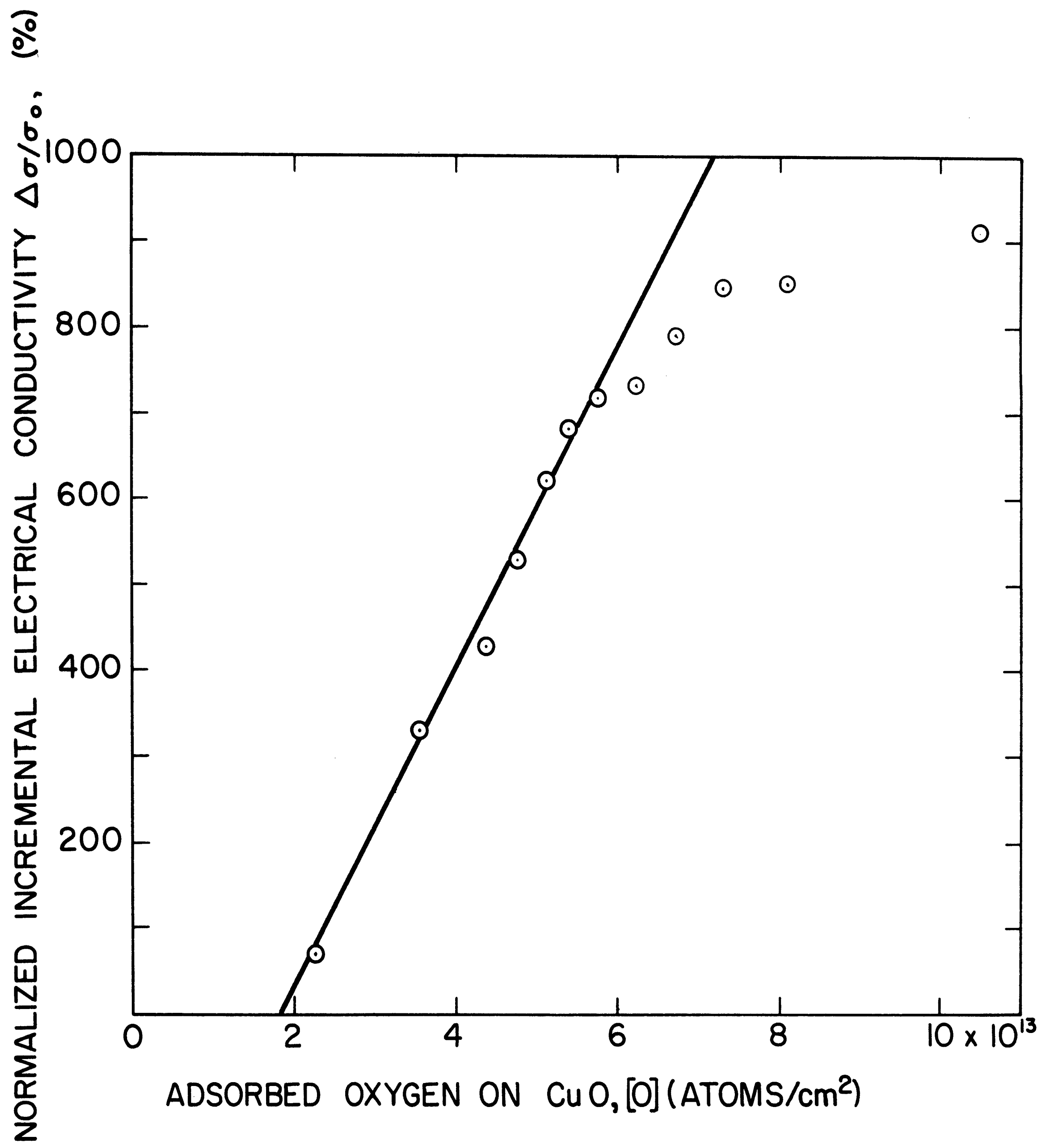

Fig. 4.5.

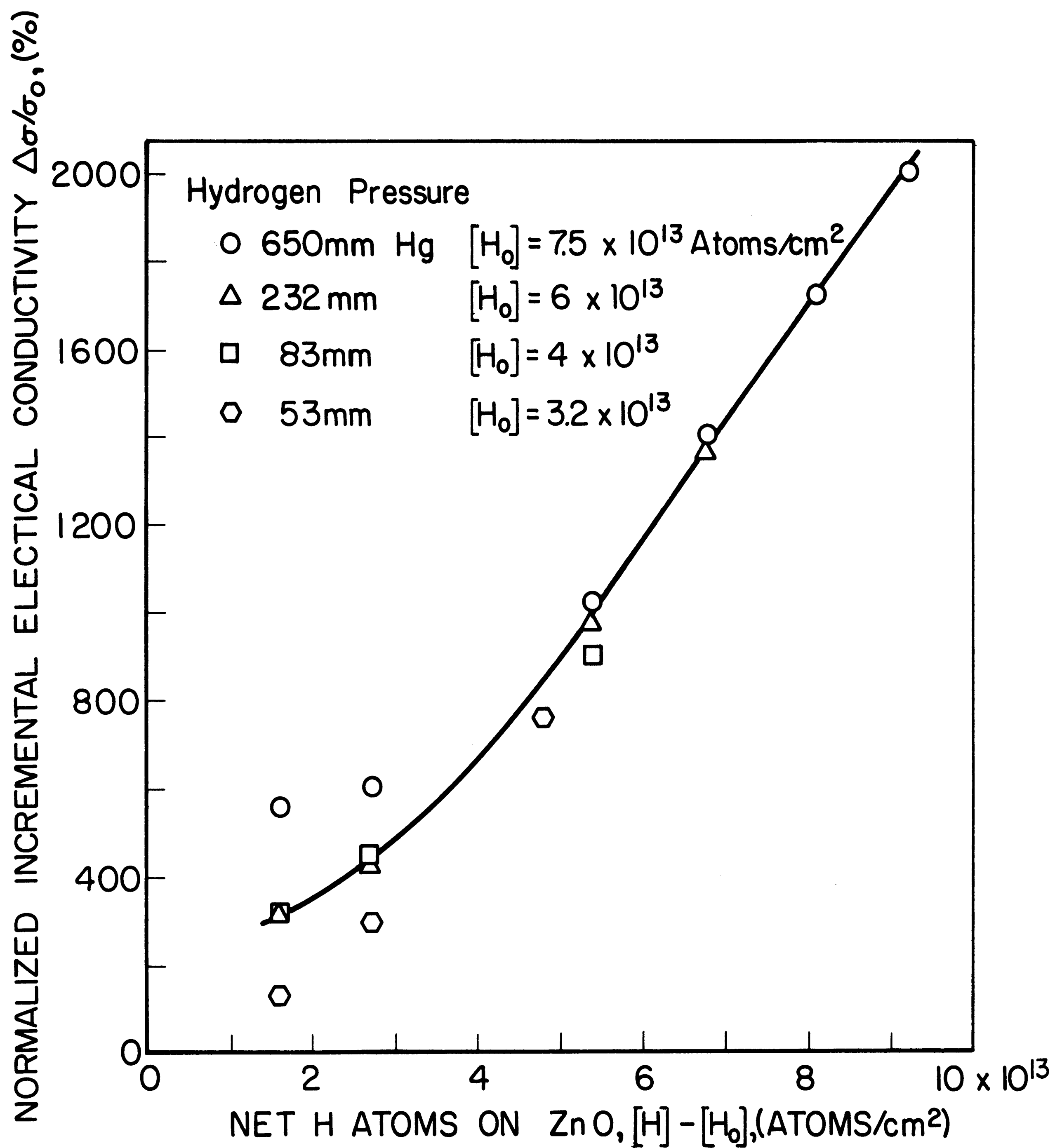

Fig. 4.6.

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