Analytical Formulation of Incremental Electrical Conductivity in Semiconductors arising from an Accumulation Space-Charge Layer*

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(Received 3 September 1963)

Analytic expressions are derived which relate 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 on different semiconducting materials. The data of Weller and Voltz for the effect of oxygen adsorbed on Cr_2O_3 do not fit the assumptions of the theory, since their particles are too small. The data of Smith for oxygen adsorbed on CuO, and the data of Molinari *et al.* 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 a definitive quantitative experimental check remains to be done, the reasonableness of the derivation has been established.

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 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 nondegenerate semiconductor material is oriented as shown in Fig. 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 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. Also, 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. Although Shrieffer[8] and Zemel[9] have shown that this is not strictly valid, it can be regarded as a zero-order approximation.

We shall now proceed to the formulation of the incremental conductivity $\Delta\sigma_s$ associated with one face of a p-type semiconductor slab as a function of surface potential and surface charge concentration arising from ionized acceptors $[A^-]$ on that face, expressed as charged centers/cm². At a distance x beneath the surface, the differential of the incremental surface conductivity is given by

$$d(\Delta\sigma_s)=q[\Delta n(x)\mu_n+\Delta p(x)\mu_p]dx. \quad (1)$$

The carrier concentrations are related to the diffusion potential $u(x)=Y(x)/kT$, where Boltzmann statistics

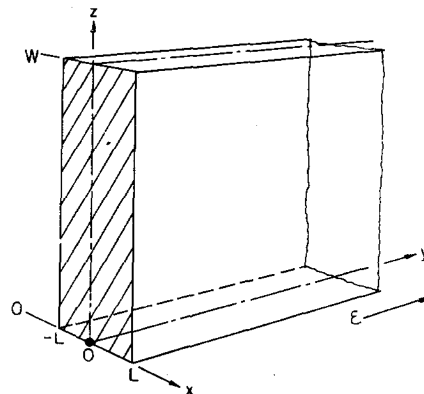

FIG. 1. Slab of semiconductor of height W and width $2L$, with electrical contacts on x–z planes and electric field $\mathcal{E}$ in the y direction.

* Contribution No. 17 from the Semiconductor Materials Research Laboratory, The College of Engineering, The University of Michigan, Ann Arbor, Michigan. This work has been supported by Texas Instruments, Inc., Dallas, Texas.

[1] C. G. B. Garrett and W. H. Brattain, Phys. Rev. **99**, 376 (1955).
[2] R. H. Kingston and S. F. Neustadter, J. Appl. Phys. **26**, 718 (1955).
[3] R. F. Greene, J. Phys. Chem. Solids **14**, 291 (1960).
[4] V. O. Mowery, J. Appl. Phys. **29**, 1753 (1958).
[5] V. B. Sandomirskii, Bulletin. Acad. Sci. USSR (English transl.) 21, 211 (1957).
[6] A. W. Smith, *Actes du Deuxieme Congres International de Catalyse, Paris, 1960* (Editions Technip, Paris, 1961), Pt. A, pp. 1711–1731.
[7] A. Cimino, E. Molinari, F. Cramarossa, and G. Ghersini, J. Catalysis **1**, 275 (1962).
[8] J. R. Schrieffer, Phys. Rev. **97**, 641 (1955).
[9] J. N. Zemel, Ann. N. Y. Acad. Sci. **101**, 830 (1963).

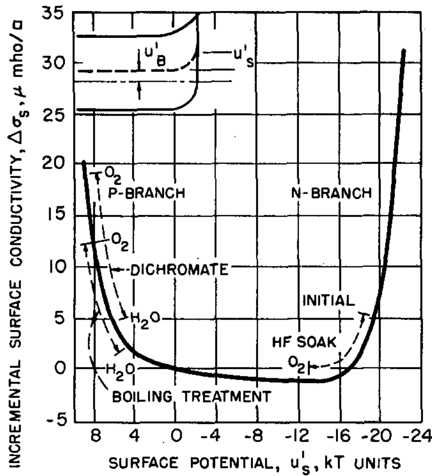

FIG. 2. Incremental surface conductivity as function of surface potential on 140-Ω-cm p-type silicon (adapted from Buck and McKim, Ref. 10).

are used in the relationships

$$\Delta n(x)=n_B \exp[u(x)]-n_B, \quad (2)$$
$$\Delta p(x)=p_B \exp[-u(x)]-p_B,$$

$u(x)$ being defined as positive when the space-charge region becomes more n type. Since surface acceptors create a more p-type space-charge region, the accompanying diffusion potential is negative. Therefore, in order to deal with positive values of the diffusion, surface, and bulk potentials in the equations, primed values are defined such that $u'(x)=-u(x)$; $u_s'=-u_s$; $u_B'=-u_B$.

In the interior of the semiconductor, wherein $u(x)=0$, then

$$\sigma_0=q[n_B\mu_n+p_B\mu_p]. \quad (3)$$

The incremental surface conductivity at a point x then can be defined as

$$d(\Delta\sigma_s)=q\{\mu_n n_B[\exp(-u')-1] + \mu_p p_B[\exp(u')-1]\}dx. \quad (4)$$

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

Mathematical Formation

The general problem can be delineated more clearly by referring to Fig. 2 adapted from Buck and McKim[10] 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 not be expected to occur until the inverted surface potential is greater than twice the bulk diffusion potential. When the surface is sufficiently 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, but the limits of integration for the diffusion potential are not so apparent. In the remaining derivations, only the accumulation is considered.

By defining

$$q(\mu_n n_B+\mu_p p_B)=2\sigma_M \cosh\theta, \quad (5)$$

$$q(\mu_p p_B-\mu_n n_B)=2\sigma_M \sinh\theta, \quad (6)$$

$$\sigma_M=qni(\mu_n\mu_p)^{\frac{1}{2}}, \quad (7)$$

$$\exp\theta=(\mu_p p_B/\mu_n n_B)^{\frac{1}{2}}, \quad (8)$$

then Eq. (4) can be written as

$$d(\Delta\sigma_s)=2\sigma_M[\cosh(\theta+u')-\cosh\theta]dx. \quad (9)$$

The total increment of current is the integral of the incremental current density over the half-width of the slab. The variable of integration in Eq. (9) can be changed from x to u'. Lee and Mason[11] showed that for accumulation layers and for highly inverted layers,

$$du'/dx=-4(L_m p_B)^{\frac{1}{2}} \sinh(u'/2), \quad (10)$$

where $L_m=2\pi q^2/\epsilon kT$.

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 Eq. (10) to a positive sign. Equation (10) 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). Substitution of Eq. (10) into Eq. (9) then gives

$$\Delta\sigma_s \cong \frac{2\sigma_M}{4(L_m p_B)^{\frac{1}{2}}} \int_0^{u_s'} \frac{[\cosh(\theta+u')-\cosh\theta]du'}{\sinh(u'/2)}, \quad (11)$$

where the appropriate boundary conditions have been substituted.

[10] T. M. Buck and F. S. McKim, J. Electrochem. Soc. **105**, 709 (1958).

[11] V.-J. Lee and D. R. Mason, J. Appl. Phys. **34**, 2660 (1963).

The integral in Eq. (11) can be simplified with hyperbolic trigonometric identities and integrated.

$$\Delta\sigma_s=\frac{8\sigma_M}{4(L_m p_B)^{\frac{1}{2}}}\int_0^{u_s'/2}\sinh(\theta+u'/2)d(\theta+u'/2)$$

$$=\frac{2\sigma_M}{(L_m p_B)^{\frac{1}{2}}}\{\cosh(\theta+u_s'/2)-\cosh(\theta)\}. \quad (12)$$

Note that when $u_s'=0$, then $\Delta\sigma_s=0$, which is required from the boundary conditions. Equation (12) can also be written as

$$\Delta\sigma_s=\frac{2\sigma_M}{(L_m p_B)^{\frac{1}{2}}}\times\{2\cosh\theta\sinh^2(u_s'/4)+\sinh\theta\sinh(u_s'/2)\}. \quad (13)$$

These equations relate the incremental surface conductivity of the accumulation layer on the surface of the semiconductor to the surface potential and the bulk properties.

Relationships to Surface Ion Concentrations

This equation now can be extended to define the incremental electrical conductivity in terms of the surface charge concentration. Lee and Mason[11] have also shown that, in general, the surface potential can be related to the surface ion concentration by the relationship

$$\sinh(u_s'/2)=(L_m/p_B)^{\frac{1}{2}}[A^-]/2. \quad (14)$$

By using Eqs. (5)–(7) and (14) and additional hyperbolic transformations, it follows that

$$\Delta\sigma_s=\frac{q(\mu_p p_B+\mu_n n_B)}{(L_m p_B)^{\frac{1}{2}}}\left\{[1+(L_m/p_B)[A^-]^2/4]^{\frac{1}{2}}-1+\frac{(L_m/p_B)^{\frac{1}{2}}(\mu_p p_B-\mu_n n_B)}{2(\mu_p p_B+\mu_n n_B)}[A^-]\right\}. \quad (15)$$

Using the model defined in Fig. 1 and Eq. (3), the fractional change in total conductivity is

$$\frac{\Delta\sigma_s}{L\sigma_0}=\frac{\Delta\sigma}{\sigma_0}=\frac{\Delta I}{I_0}=\frac{1}{L(L_m p_m)^{\frac{1}{2}}}\left\{[1+(L_m/p_B)[A^-]^2/4]^{\frac{1}{2}}-1+\frac{(L_m/p_B)^{\frac{1}{2}}(\mu_p p_B-\mu_n n_B)}{2(\mu_p p_B+\mu_n n_B)}[A^-]\right\}. \quad (16)$$

Simpler relationships can be obtained for high surface coverage and low surface coverage.

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%, and Eq. (13) can be written

$$\Delta\sigma_s=\frac{2\sigma_M}{(L_m p_B)^{\frac{1}{2}}}\{(\cosh\theta+\sinh\theta)\sinh(u_s'/2)\}. \quad (17)$$

Substitution of Eqs. (5)–(7) gives

$$\Delta\sigma_s\cong q\mu_p[A^-]. \quad (18)$$

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

The fractional change in total conductivity is

$$\left(\frac{\Delta\sigma}{\sigma_0}\right)=\left(\frac{\Delta I}{I_0}\right)=\frac{\mu_p[A^-]}{L(\mu_n n_B+\mu_p p_B)}. \quad (19)$$

For semiconductors, wherein the electron contribution to the total conductivity is negligible, then Eq. (19) becomes

$$(\Delta\sigma/\sigma_0)=(\Delta I/I_0)=[A^-]/Lp_B. \quad (20)$$

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

Low Surface Coverage ($u_s'\leq 1$)

For low surface coverage, when $u_s'\leq 1$, then $\sinh(u_s'/2)\simeq(u_s'/2)$ within 4%. Similarly,

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

Equation (13) gives the incremental surface conductivity as

$$\Delta\sigma_s=\frac{q}{2p_B}\left\{\frac{(\mu_p p_B+\mu_n n_B)(L_m/p_B)^{\frac{1}{2}}}{4}[A^-]^2+(\mu_p p_B-\mu_n n_B)[A^-]\right\}. \quad (21)$$

The fraction change in total conductivity is

$$\left(\frac{\Delta\sigma}{\sigma_0}\right)=\left(\frac{\Delta I}{I_0}\right)=\frac{1}{2Lp_B}\left\{\frac{(L_m/p_B)^{\frac{1}{2}}}{4}[A^-]^2+\left(\frac{\mu_p p_B-\mu_n n_B}{\mu_p p_B+\mu_n n_B}\right)[A^-]\right\}. \quad (22)$$

This expression and Eq. (16) are 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.

The above formulations are for an intrinsic or p-type semiconductor with a negative surface charge. The re-

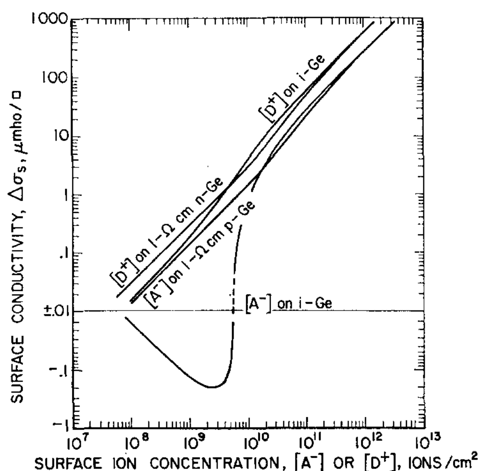

FIG. 3. Computed relationships between $\Delta\sigma_s$ and surface ion concentrations on germanium at 300°K.

sults 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. An analytic relationship which gives the same results for accumulation layers is represented by Eq. (13) above. Mowery has also presented a graphical correlation between surface charge and surface potential for germanium and silicon. These same results are expressed in analytic form for accumulation layers on any semiconductor by Eq. (14) 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.

The p branch of the relationship between $\Delta\sigma_s$ and u_s' shown in Fig. 2 can be computed from Eq. (12), and the agreement appears to be within $\pm 20\%$ from the published curve. A more precise comparison with a curve derived for 15 000 Ω·cm p-type silicon showed an average variation of about $\pm 25\%$. These comparisons then constitute 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 Fig. 3, Eq. (15) is plotted showing $\Delta\sigma_s$ as a function of ionized surface acceptor concentration $[A^-]$ on intrinsic and 1 Ω·cm p-type germanium. Similar curves are also shown for ionized surface donor concentration $[D^+]$ on intrinsic and 1 Ω·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 Fig. 3.

Experimental Evaluation

Three sets of experimental data are available[6,7,12] which may be used to ascertain the validity of the theories presented above. Although none of these works gives a good quantitative check of the theories in all aspects, the observed trends are semiquantitatively correct. Each set of data is discussed separately.

Smith[6] has published data showing changes in conductivity in thin films of CuO as a function of oxygen adsorbed on the surface. However, it is difficult to ascertain exactly what the author has done experimentally, and his theoretical 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/cm², that his reference conductance (g_0) for film 3 is 44 μmho for the conditions reported in Smith's Fig. 4, and that the film thickness of film 3 is 0.1 μ. We have further assumed that the reported measurements of conductance as a function of surface coverage were made at 127°C (not critical). With these assumptions Smith's data are plotted in Fig. 4 showing $\Delta\sigma/\sigma_0$ as a function of adsorbed oxygen concentration [O].

Smith observes that some oxygen is adsorbed immediately which has no influence on the film conduc-

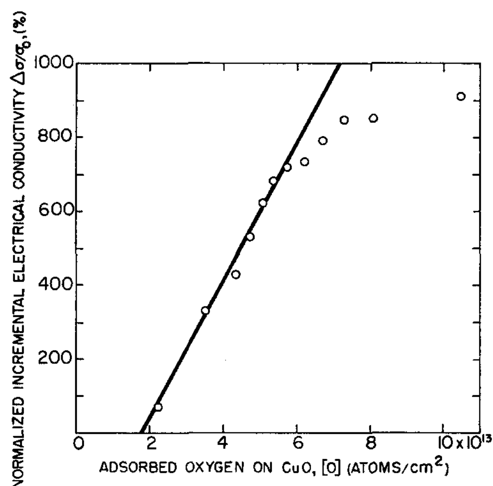

FIG. 4. Normalized incremental electrical conductivity of a CuO film as a function of surface oxygen concentration (after Smith).

[12] S. W. Weller and S. E. Voltz, *Advances in Catalysis* (Academic Press Inc., New York, 1957), Vol. 9, pp. 215–223.

tance. These atoms presumably form a nonionic surface dipole layer, or fill covalent surface states, but do not ionize or 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 as expected from Eq. (20).

By making an approximate computation using an as yet unpublished adsorption theory,[13] and assuming a shallow surface acceptor level, then it appears that most of the oxygen atoms on the surface are singly ionized. With this assumption, the slope of the line in Fig. 4 indicates that $p_B=5\times10^{17}$ 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, $\sigma_0=0.176$ mho/cm, from which it follows that the hole mobility $\mu_p\simeq2$ cm^2/V·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 $L_m=3\times10^{-6}$ cm, the screening length, $L_s=\frac{1}{2}(L_mp_B)^{\frac{1}{2}}=4\times10^{-7}$ 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. If the monolayer coverage is greater than 2×10^{14} atoms/cm^2, the magnitudes of these conclusions will not be grossly affected.

Cimino *et al.*[7] have measured changes in the electrical conductivity of compressed beds of ZnO 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

$$\Delta\sigma_{s,1}-\Delta\sigma_{s,0}=\Delta\chi hd/4S, \tag{23}$$

where $\Delta\sigma_{s,1}$ is the final surface conductance, mho/square; $\Delta\sigma_{s,0}$ is the reference surface conductance, mho/square; $\Delta\chi$ is the reported conductance change, mho; h is the distance between platinum contacts, cm; d is the average particle dimension, cm; and S is the 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/g. For a surface roughness factor of 2, then $d\simeq4\times10^{-4}$ 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

[13] V.-J. Lee, Ph.D. thesis, University of Michigan, Ann Arbor, 1962.

[14] Pekar, quoted in A. F. Ioffe, *Physics of Semiconductors* (Academic Press Inc., New York, 1960), pp. 178–179.

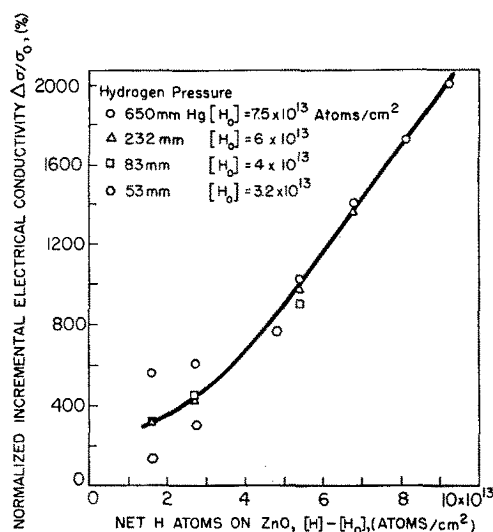

FIG. 5. Normalized incremental electrical conductivity of compressed ZnO powder as a function of surface oxygen concentration (after Cimino *et al.* Ref. 7).

the reference conditions have been established as a result of initial gas uptake.

For ZnO heat treated in vacuum, the reference conductance was measured as a function of temperature. At 57°C, $\chi_0\simeq10^{-5}$ mho. After subtracting out the initial amount of hydrogen adsorbed at various pressures, their data at 57°C showing $\Delta\chi/\chi_0$ vs net adsorbed hydrogen concentration are given in Fig. 5. From the high coverage theory give in Eq. (20) and adapted to n-type material, it follows that

$$\Delta\chi/\chi_0=\Delta\sigma/\sigma_0=\{[\mathrm{H}]/Ln_B\}\{[\mathrm{H}^+]/[\mathrm{H}]\}. \tag{24}$$

Since $L\simeq d/2$, then

$$n_B/\{[\mathrm{H}^+]/[\mathrm{H}]\}=2[\mathrm{H}]\chi_0/d\Delta\chi=2.3\times10^{16}. \tag{25}$$

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 Eqs. (18) and (24), then

$$\Delta\sigma_s=\frac{\Delta\chi hd}{S}=q\mu_n[\mathrm{H}]\{[\mathrm{H}^+]/[\mathrm{H}]\} \tag{26}$$

or

$$\mu_n=\frac{\Delta\chi d}{q[\mathrm{H}]\{[\mathrm{H}^+]/[\mathrm{H}]\}}=5.4\times10^{-3}\ \mathrm{cm^2/V\cdot sec}. \tag{27}$$

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

$$\chi_0=\sigma_0S/h=(S/h)(n_Bq\mu_n)=10^{-5}\ \mathrm{mho}. \tag{28}$$

Using the assumptions and conclusions above it is found that $\mu_n\simeq2.7\times10^{-3}$ cm^2/V·sec which agrees within a factor of 2 of the value found from the incremental conductivity theory above. This can be com-

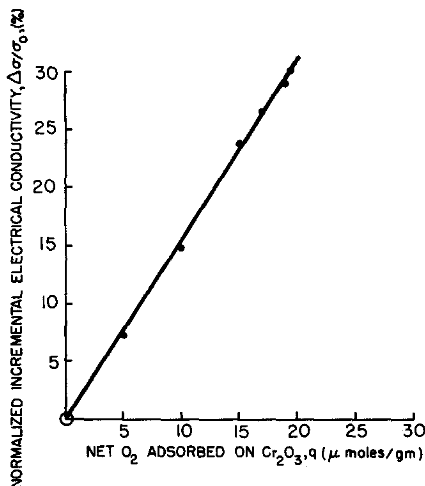

FIG. 6. Normalized incremental electrical conductivity increase of sintered Cr_2O_3 as function of amount of adsorbed oxygen (after Weller and Voltz, Ref. 12).

pared with a value of about 100 cm²/V·sec for single crystals of ZnO, so that this indicates a large decrease in mobility in the compressed particles form of the material.

These data indicate that $L_m = 4\times10^{-6}$ cm. At the beginning of the linear region (5×10^{13} ions/cm²), Eq. (14) indicates that $u_s = 13$, which supports the assumption of conditions of high surface coverage.

Weller and Voltz[12] 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 in Fig. 6 show $\Delta\sigma/\sigma_0$ as a function of net O_2 adsorbed in micromoles/g. In another publication,[15] they reported that the surface area of this material was equal to 35 m²/g. 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 μ. The data from Fig. 7 show that

$$(\Delta\sigma/\sigma_0) = 4.4\times10^{-15}[\mathrm{O}]([\mathrm{O}^-]/[\mathrm{O}]) = [\mathrm{O}^-]/Lp_B, \quad (29)$$

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. A comparison of this result with Eq. (20) shows that p_B is equal to about 10^{19} holes/cm³.

Weller and Voltz also report an original "conductivity" σ_0, in the absence of adsorbed oxygen, as 1.4×10^{-4} Ω·cm. This presumably is for the particulate solid, and should be somewhat greater for a homogeneous solid. However, using this value of σ_0 with the hole concentration obtained above, it follows that the hole mobility $u_p \simeq 10^{-3}$ cm²/V·sec at 500°C. 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[16] 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/cm³ and the Hall mobility was 2 cm²/V·sec at 442°C. Therefore, it appears that the hole mobility obtained in this work may be somewhat low.

Chapman *et al.* have also shown that from 400° to 500°C, 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 and 2.86 eV were obtained on materials annealed in hydrogen and vacuum, respectively.

By assuming that the concentration of acceptor levels is 3×10^{20}/cm³ (from 75 μ moles excess O_2/g, 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 $4.83\times10^{15}\,T^{\frac{3}{2}} \simeq 10^{20}$, then it follows that the Fermi level is at $E_a/2$, and $p_B \simeq 10^{16}$ holes/cm³. The agreement with the previously ascertained value of 10^{19} holes/cm³ is poor. For $\Delta\sigma/\sigma_0 = 0.1$, 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 $[L_s = \frac{1}{2}(L_m p_B)^{\frac{1}{2}} = 5\times10^{-6}$ cm$]$.

[15] S. E. Voltz and S. Weller, J. Am. Chem. Soc. 75, 5231 (1953).

[16] P. R. Chapman, R. H. Griffith, and J. D. F. Marsh, Proc. Royal Soc. (London) A224, 419 (1954).