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Hydrogen Chemisorption and Electrical Conductivity of Zinc Oxide Semiconductors

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The influence of hydrogen chemisorption on the electrical conductivity of zinc oxide powders has been investigated in the temperature range 0°–350°C, at hydrogen pressures between 30 and 500 torr. Pure zinc oxide, as well as samples containing Ga^{3+} (0.7%) and Li^{+} (1.0%) have been studied. Electrical conductivity increases ($\Delta\chi$) have been correlated with amounts of hydrogen chemisorbed (q) on the basis of previous studies of chemisorption kinetics. Observed $\Delta\chi$'s for a given q, increase with increasing temperature. They vary with q in a complex manner (dependent upon temperature). At constant temperature, the $\Delta\chi$ observed for a given q depends upon the pressure at which hydrogen had been adsorbed. At constant q, observed $\Delta\chi$'s decrease in the order: $ZnO + Ga_2O_3$, ZnO, $ZnO + Li_2O$. The results are discussed on the basis of a previously proposed chemisorption model. Other possible interpretations are also examined.

Electrical conductivity measurements have often been utilized as an auxiliary means in the study of catalytic or chemisorption processes occurring on the surface of a solid. In this paper we shall report the results of an investigation on the influence of hydrogen chemisorption on the electrical conductivity of zinc oxide powders, pure or with the addition of Ga^{3+} or Li^{+}. The kinetics of hydrogen chemisorption on the same type of zinc oxide semiconductors was previously investigated in this laboratory (*1, 2, 3*), and a mechanism was proposed (*4*).

The influence of hydrogen on the electrical conductivity of zinc oxide was previously investigated by several authors. These studies, recently reviewed by Heiland, Mollwo, and Stöckmann (*5*), can be divided into two groups: (a) single crytals; (b) powders (and films). In single crystals the surface-to-volume ratio is low, hence the electrical behavior is governed by bulk phenomena, except at low temperatures (generally below room temperature). In a few cases only the surface contribution becomes apparent above room temperature. In powders, surface effects predominate even above room temperature, in a temperature range where chemisorption phenomena are important and better studied. This type of a system therefore lends itself to a study of surface phenomena. However, the complexity of the powder systems only allows qualitative conclusions to be drawn.

Hydrogen chemisorption has been found to increase the electrical conductivity of zinc oxide powders at sufficiently high temperatures (*6, 7*). Different interpretations of this effect have been offered, which stem from two points of view. Some authors (*4, 6, 7, 9, 11*) ascribe the electrical conductivity increase to the presence of two (or more) types of chemisorbed hydrogen. According to others (*8, 10*), hydrogen would be only indirectly responsible for the increase of conductivity. The increase would be caused by a reduction of the oxide, leading to excess zinc. It is the purpose of this paper to examine in more detail various factors which determine the influence of hydrogen on the electrical conductivity. The results also allow us to clarify some aspects of the mechanism previously proposed for the chemisorption of hydrogen on zinc oxide (*4*).

EXPERIMENTAL METHODS

The conductivity cell is similar to that described by Garner and Haycock (*12*), except for a modification regarding the upper electrode. This is made of a flat spiral of platinum wire, embedded in the powder at a depth of about 0.5 cm. In our cell the magnetically driven piston rests on the top of the powder during measurements. For the present research the system has been found to be fully satisfactory.

The cell was connected to a high vacuum system ($\sim 10^{-5}$ torr), to gas reservoirs, mercury manometers, and Pirani and Philips gauges. The cell could fit vertically into the hole of a mobile furnace, made of a large block of aluminum. Temperatures were kept constant (±1°C) by means of a resistance thermoregulator and read by means of a Chromel-Alumel thermocouple, held against the external wall of the cell. No thermal gradient was present in the sample zone. Electrical conductivities down to 10^{-10} mhos, were measured by means of an ac (1592 c/s) bridge (Wayne-Kerr B 221), with a precision of ±0.2% from 111 mmhos to 0.01 mhos. For comparison, some dc measurements have also been carried out by means of a Wheatstone bridge for high resistivities (Pye 7436). For the preparation and pretreatment of the samples, see reference (*2*). Some experiments carried out with hydrogen purified through a palladium valve gave the same results.

EXPERIMENTAL RESULTS

The experimental results can best be illustrated by means of graphs. The graphs shown refer to individual samples, and are representative of the behavior of each type of solid at the specified conditions. Reproducibility within each sample is generally better than ±5%. Conductivities shown are measured with an ac bridge.

A comparison between ac and dc measurements shows that conductivity variations $\Delta\chi$ are the same in ac or dc providing the initial conductivity of the activated sample is higher than about 10^{-5} mhos. At lower conductivities the two methods give values of $\Delta\chi$ which may differ by about 15%.

When conductivities are lower than about 10^{-5} mhos, voltage–intensity curves reveal the presence of nonohmic contacts. Nonohmicity increases with decreasing conductivity.

Activation Process

In order to obtain an active and reproducible sample, a conditioning treatment of the surface has to be carried out. This activation process should be examined in some detail before the influence of hydrogen is discussed. It may be recalled that activation of the surface of zinc oxide is a necessary step for chemisorbing hydrogen, or for obtaining good catalytic activity in the H_2–D_2 exchange reaction. The activation process requires heating the sample under good vacuum at about 400°–450°C. Good catalytic activity for the H_2–D_2 exchange reaction can also be reached by hydrogen treatment at around 350°C. All our samples have undergone a vacuum treatment at 450°C before each experiment, unless otherwise stated. The electrical conductivity of the fresh sample has been followed during the first and successive activations as a function of temperature. It has been found that successive treatments progressively increase the value of the electrical conductivity of all samples (pure and doped) in the whole temperature range investigated. (Lithium-containing samples are an exception below 150°C. Their behavior will be discussed elsewhere). Correspondingly, the temperature coefficient E of electrical conductivity decreases. Values of χ and E obtained after activations which followed hydrogen treatment can be considered as limiting values for the activation process. Subsequent activations of the sample only result in modest variations of χ and E.

The activation process is clearly linked to the destruction of the surface depletion layer created by chemisorbed oxygen. This layer is partly responsible for the low conductivity of fresh samples. The activation process, beside removing the depletion layer can also lead to a surface richer in zinc, by elimination of oxygen atoms from surface lattice positions. The removal of surface oxygen thus also consists in a surface reduction of the oxide. It should be recalled at this point that the composition of the defective oxide surface can vary with pretreatments and with the nature and pressure of the surrounding gas. It is worth considering some experimental evidence which limits the importance of a possible reduction process. As noted before, it is found that the activation process reaches a fairly reproducible and constant limit. In addition, it has been found by Heiland (*11*) that quite different hydrogen treatments—a few minutes at 500°C, 6 or 25 atm, or a few seconds at 800°C, 1 atm—lead to electron concentrations comprised within a factor of 5. One is then led to the conclusion that while the removal of surface oxygen from a fresh sample entrains marked variations of the properties of the oxide surface, further and even drastic oxygen elimination can not vary the defective properties beyond a certain limit.

Pure Zinc Oxide

Sintered zinc oxide has been mainly studied. The behavior of unsintered oxide is similar, but its study is more difficult because of the variation of surface area during pretreatments [see Eq. (4)]. Figure 1 shows conductivity changes $\Delta\chi$ during heating and successive cooling in air, under vacuum, or in hydrogen. One can notice the steep rise of conductivity occurring above 300°C in air or under vacuum, and the different behavior upon cooling. Under vacuum, high values of χ are maintained upon cooling, log χ vs. $1/T$ plots are linear with E values of about 5 kcal/mole, and the behavior of the sample is reversible. In air, χ drops again to low values upon cooling. Above approximately 150°C, rising and falling temperature curves are practically superposed, but below 150°C the behavior is more complex. Adsorption phenomena which depend on the state of the surface greatly influence the low temperature behavior. They have been investigated by us and will be discussed elsewhere.

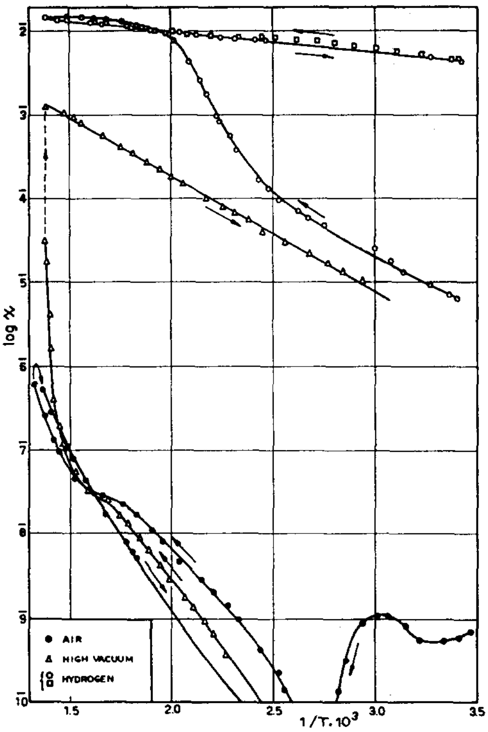

FIG. 1. Conductivity as a function of temperature for sintered ZnO. Heating and cooling curves in air, vacuum, or hydrogen.

If hydrogen is admitted at room temperature to an activated sample, a steep rise of χ is observed upon first heating the sample. Successive descents and ascents are linear, with E values of the order of 0.3 kcal/mole. Values of χ remain therefore high in the whole temperature range. As already noted, evacuation at 400–450°C of a hydrogen-treated sample restores the behavior of the activated sample, with only a slight change in E and χ, compared to a nontreated sample.

Conductivity and surface coverage. If hydrogen is admitted at constant temperature, a time dependent increase of χ is observed, shown in Figs. 2a and 2b, for temperatures below, and, respectively, above 110°C. Of more interest is the correlation between $\Delta\chi$ and chemisorbed amounts, q. This correlation was obtained by calculating q as a function of time. The calculation was possible because the samples employed in this research are the same as those previously investigated for kinetic studies. It can be recalled that the chemi-

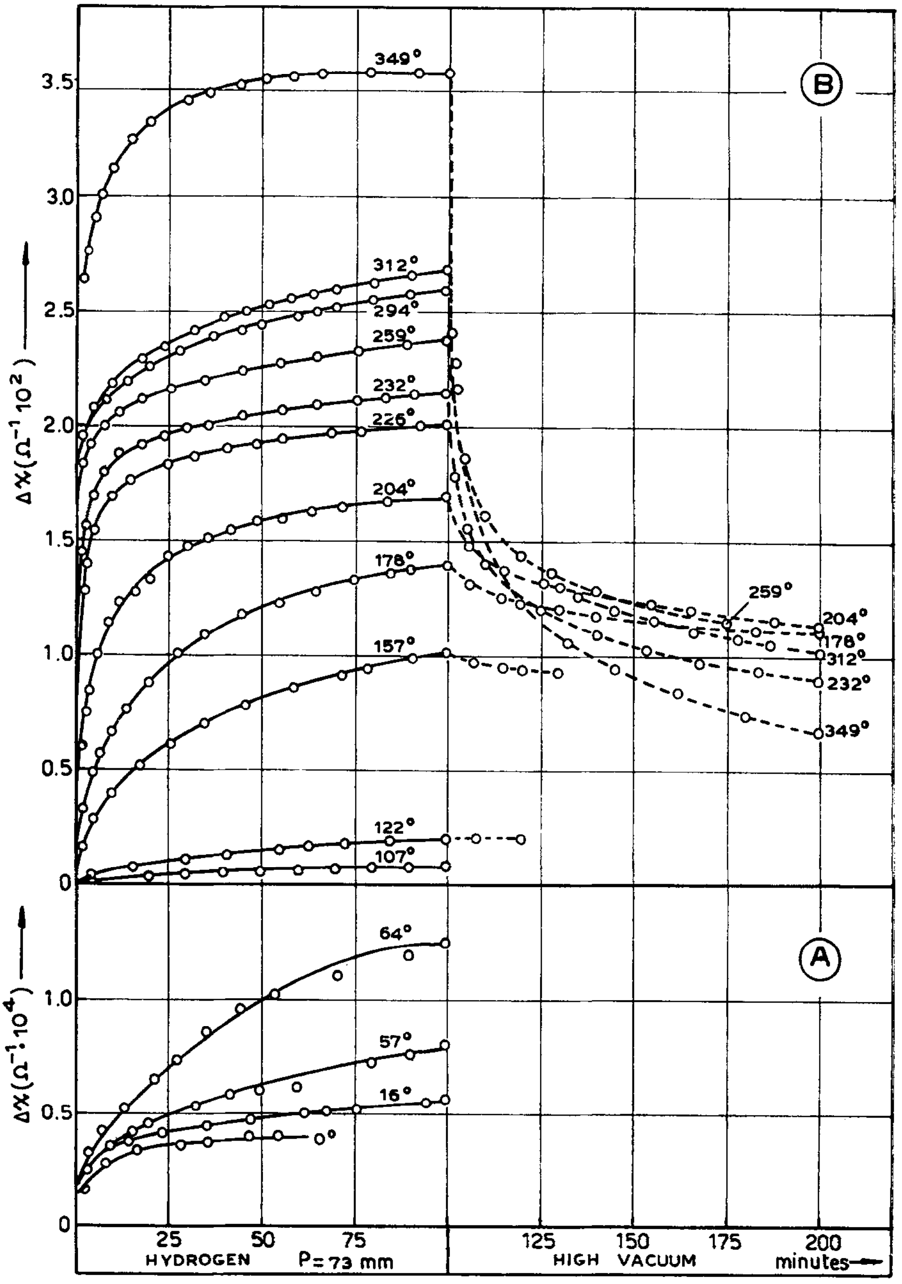

FIG. 2. Sintered ZnO. Conductivity changes upon admission of H_2 (73 torr) at constant temperature (full lines), and subsequent evacuation (dashed lines).

sorption kinetics conforms to the Elovich equation (*1, 4*):

$$q = (2.3/\alpha)(\log (t + t_0) + \log a\alpha)$$

Chemisorbed amounts can then be computed once the kinetic parameters are known. Knowledge of apparent "orders" of the kinetic parameters allows us to compute the time dependence of q at the pressure prevailing during conductivity measurements. It should be stressed that the limits of errors within which the kinetic parameters can be evaluated are such as to give a significant correlation curve between $\Delta\chi$ and q. Simultaneous measurements of $\Delta\chi$ and q at a few temperatures, performed in our laboratory in the course of different research, confirm calculated behaviors. A confirmation of the low temperature behavior also comes from the work of Barry and Klier (*9*). It should be remembered that the chemisorption kinetics can be determined only after the very rapid adsorption of an initial amount $q_i \neq 0$, adsorbed in less than 15 sec. It is therefore impossible to trace $\Delta\chi$ vs. q curves for $q < q_i$. Figures 3a and 3b show the curves obtained at different temperatures, at a pressure of 73 torr. They clearly show the marked dependence upon T of the conductivity changes $\Delta\chi$ brought about by equal amounts q. An additional feature which should be noticed is the disproportionate effect of surface coverage on χ. At low temperatures, hydrogen chemisorbed at high coverages is more effective in causing conductivity increases. At high temperatures, $d\chi/dq$ decreases as the coverage increases.

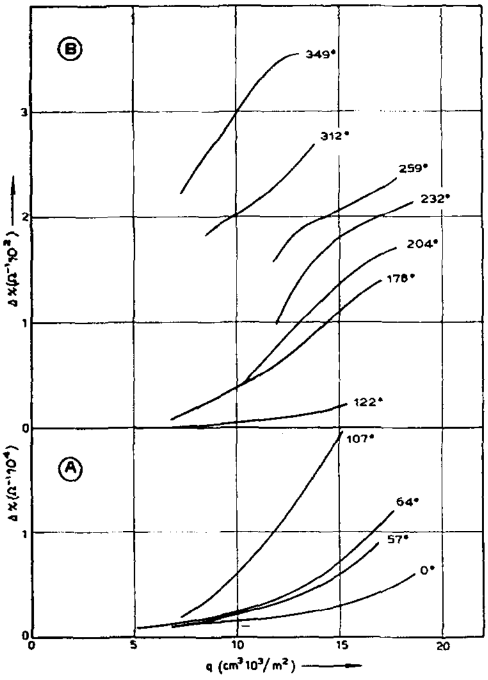

FIG. 3. Sintered ZnO. Conductivity changes as a function of amount of hydrogen chemisorbed at constant temperature ($P_{H_2} = 73$ torr).

Hydrogen desorption. Desorption measurements have previously shown (*4*) that about 80% of the hydrogen chemisorbed at 56°C or at 216°C is removed under vacuum at the adsorption temperature. From the curves of Fig. 2b it can be seen that when a sample is subjected to a vacuum, and therefore a considerable portion of the chemisorbed gas is removed, very little decrease of conductivity occurs at low temperatures. The decrease is more marked, the higher the temperature.

Influence of pressure. Figure 4 shows conductivity changes with time, at different pressures. Figure 5 shows the corresponding $\Delta\chi$ vs. q curves. A characteristic feature can be observed. Equal amounts of gas adsorbed at different pressures give rise to different conductivity changes. The $\Delta\chi$ brought about by a given amount q is thus not only a function of T but also of pressure. It should be noted that the observed difference is well outside possible errors in the evaluation of the curves. Figure 5 also shows $\Delta\chi$ plotted as a function of $q - q_0$, where q_0 represents an amount of gas close to the amount q_i chemisorbed during the initial rapid process which does not obey the Elovich equation (*1, 4*). The curves obtained at different pressures tend to superpose one another.

Zinc Oxide with Lithium

Figure 6 shows conductivity changes of a Li-containing sample with rising and falling temperature, in air, under vacuum, or

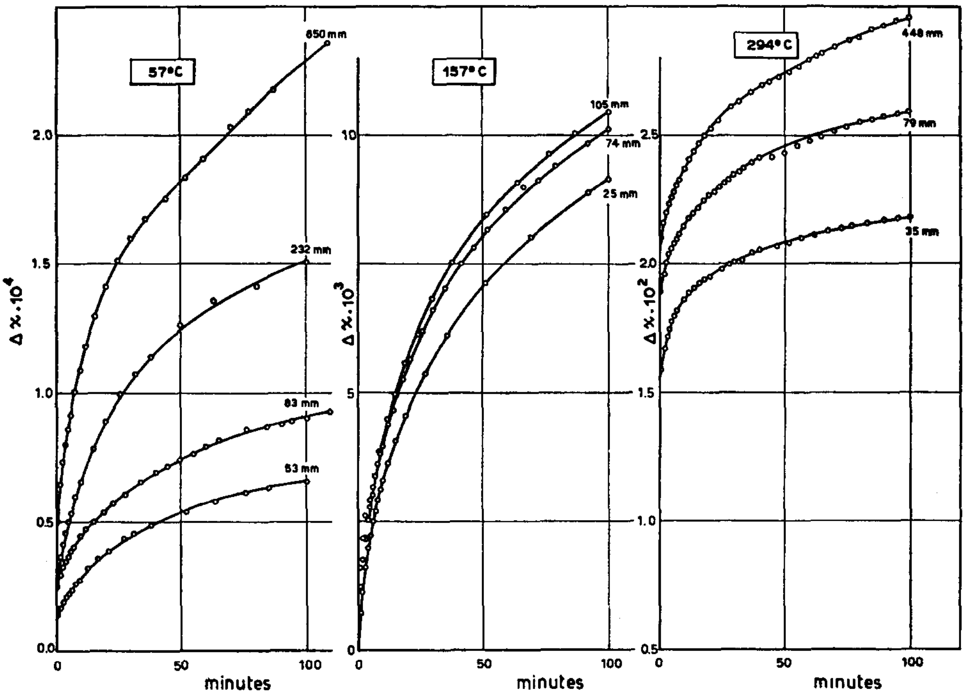

FIG. 4. Sintered ZnO. Conductivity changes upon admission of H_2 at different pressures.

in hydrogen. If hydrogen is admitted at constant temperature on an activated sample, a conductivity change can be observed, which progresses with time (Figs. 7a and b). It should be noted that the adsorption study (*2*) has shown that a measurable kinetic process could be observed only at or above 200°C. Failure to observe an adsorption kinetics, however, does not necessarily mean that gas is not being adsorbed. The total amount of gas adsorbed on these samples is small, because of the low surface area. A slow chemisorption of less than 10% of the total chemisorbed amount would then escape experimental observation. The absence of a measurable kinetic process for a wide temperature range does not permit a determination of $\Delta\chi$ as a function of q.

Zinc Oxide with Gallium

Figure 8 shows conductivity changes with rising and falling temperature in air, under vacuum, and in hydrogen. Figures 9a and 9b show conductivity changes with time, when hydrogen is admitted at 73 torr at constant temperature.

Figure 10 shows the conductivity changes with time at different pressures.

Figures 11 and 12 report the calculated $\Delta\chi$ vs. q curves, at different temperatures and pressures. Observations similar to those made for pure ZnO can be made.

A comparison of the efficiency of hydrogen in causing conductivity increases in samples of different semiconductivity is made in Fig. 13. In the figure, $\Delta\chi^*_{100}/q_{100}$ is plotted as a function of T. $\Delta\chi^*_{100}$ is the conductivity change observed after 100 minutes, corrected according to Eq. (4). This correction is made to allow for different electrode distances and particle size. The amount chemisorbed after 100 minutes is represented by q_{100}.

DISCUSSION

The data illustrated in the preceding pages show that the conductivity increase of zinc oxide caused by the interaction with hydrogen is a function of temperature,

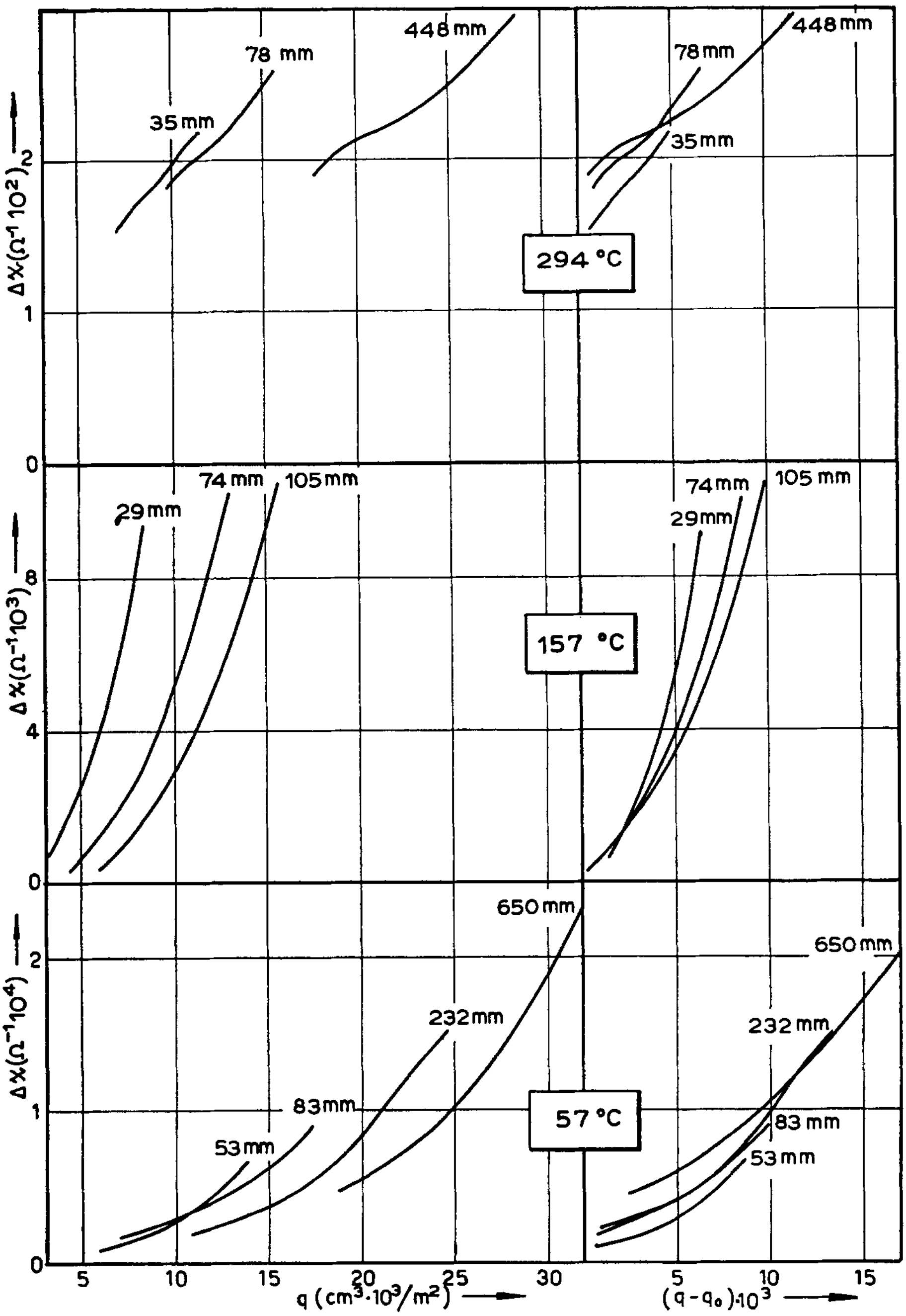

FIG. 5. Sintered ZnO. Conductivity changes as a function of: (left side) amount of hydrogen chemisorbed at different pressures; (right side) $q - q_0$ (see text).

pressure, surface coverage, and type of addition. As mentioned in the introduction, two different points of view have been adopted in discussing the effect of hydrogen on the electrical conductivity.

1. Hydrogen atoms adsorbed on the sur-

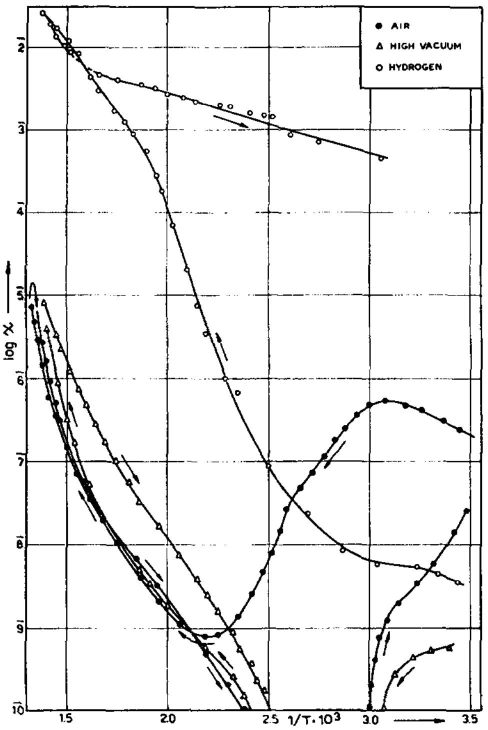

FIG. 6. Conductivity as a function of temperature for ZnO + Li_2O (0.5% molar). Heating and cooling curves in air, vacuum, or hydrogen.

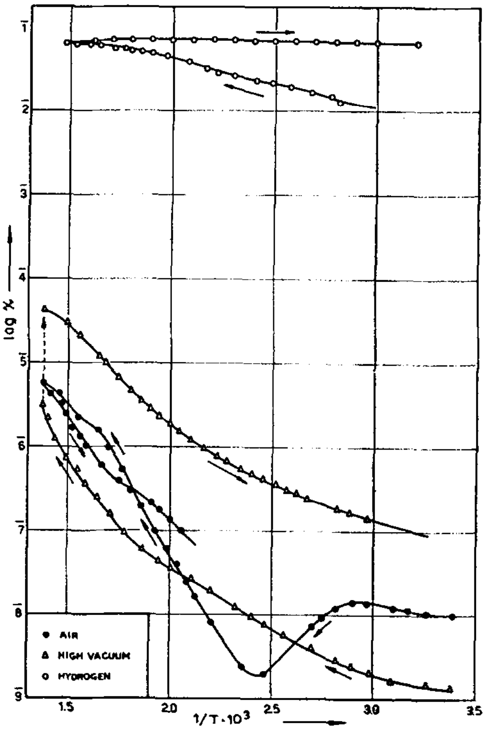

FIG. 8. Conductivity as a function of temperature for ZnO + Ga_2O_3 (0.35 molar). Heating and cooling curves in air, vacuum, or hydrogen.

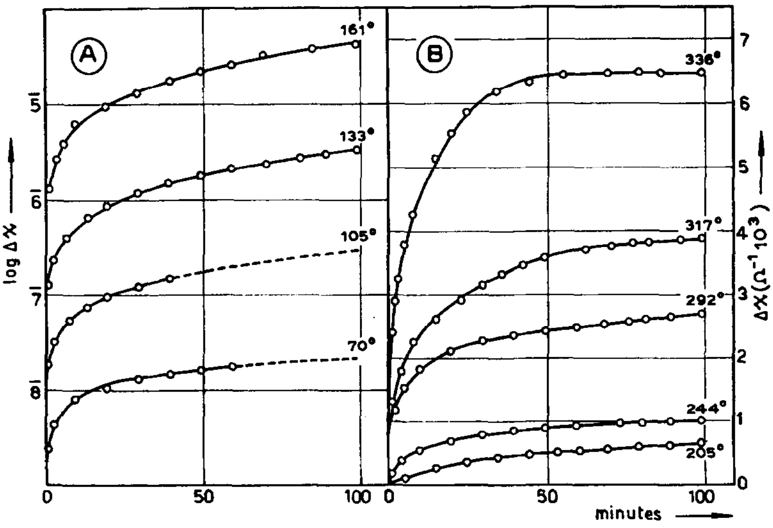

FIG. 7. ZnO + Li_2O. Conductivity changes upon admission of H_2 (70 torr) at constant temperature.

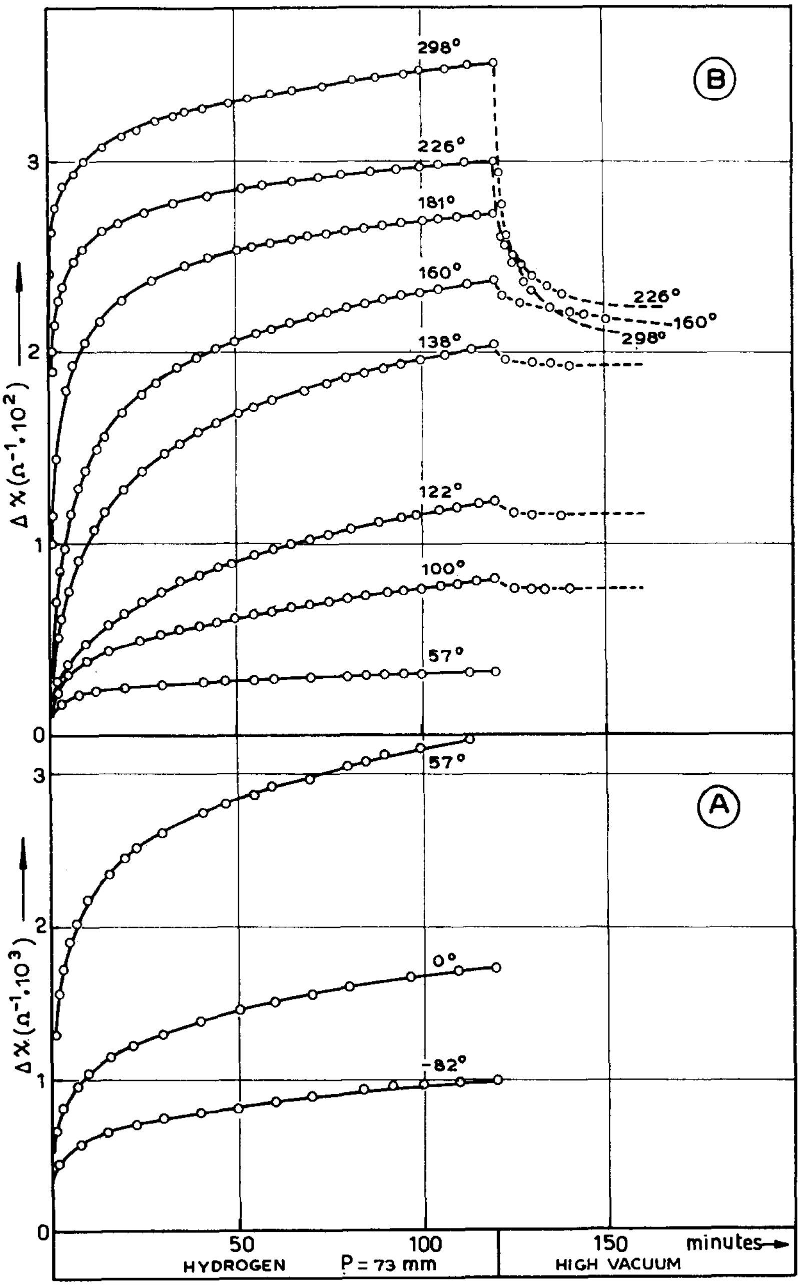

FIG. 9. $ZnO + Ga_2O_3$. Conductivity changes upon admission of H_2 (73 torr) at constant temperature (full lines), and subsequent evacuation (dashed lines).

face, represent donor centers in the energy scheme of the semiconductor. In this hypothesis it is necessary to take into account the possibility of the existence of different types of hydrogen–surface bonds, as well as the variation of the donor properties of each type of bond when the experimental conditions are changed (variation of T, p, coverage). This point of view is the one adopted here and will be discussed further

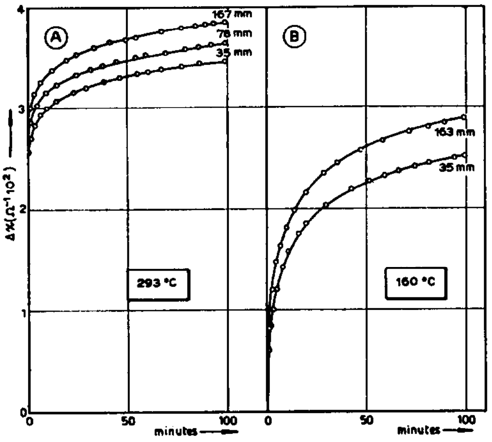

FIG. 10. ZnO + Ga_2O_3. Conductivity changes upon admission of H_2 at different pressures.

below in connection with the mechanism of hydrogen chemisorption previously outlined (*4*). The background physical scheme is essentially that discussed by Heiland, Mollwo, and Stöckmann (*5*).

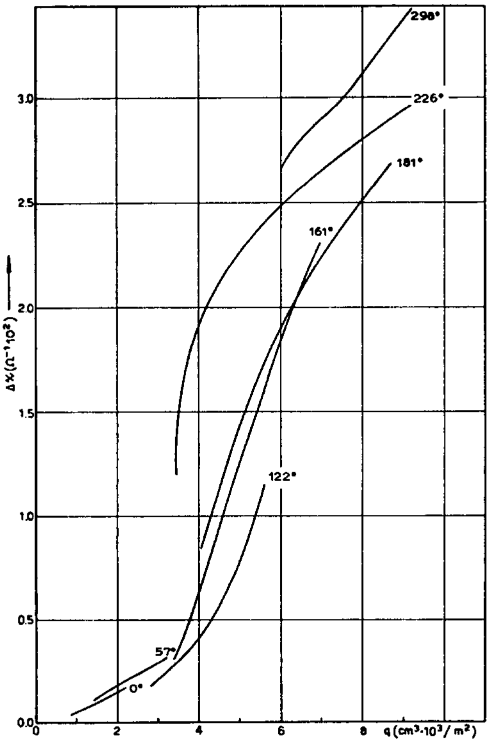

FIG. 11. ZnO + Ga_2O_3. Conductivity changes as a function of hydrogen chemisorbed at constant temperature ($P_{H_2} = 73$ torr).

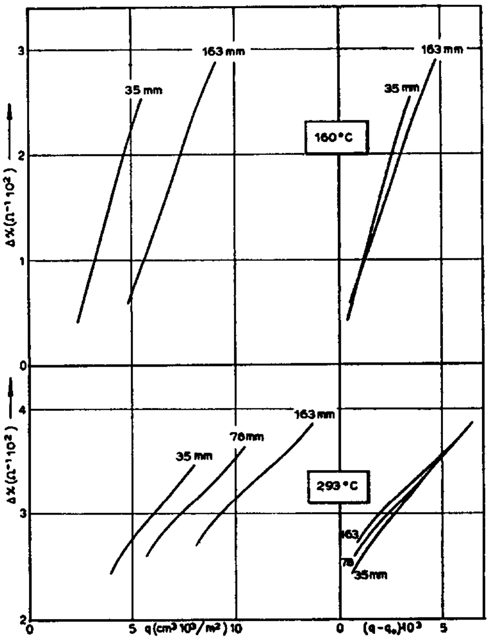

FIG. 12. ZnO + Ga_2O_3. Conductivity changes as a function of: (left side) amount of hydrogen chemisorbed at different pressures; (right side) $q - q_0$.

2. The effect of hydrogen, in the other point of view, is only indirect. Hydrogen causes surface reduction of the oxide. Reduced zinc atoms (or ions), or oxygen vacancies, act as donors.

In either case, it would be necessary to evaluate the role of electron and hole traps. These traps control the conductivity increase. The presence of traps has been clearly demonstrated by optical, electrical, and photoconductivity studies (*5*). In spite of the further complication introduced by the existence of traps, these cannot be ignored in a discussion of surface phenomena.

Hydrogen Chemisorption and Electrical Conductivity

Outline of the proposed chemisorption mechanism. It is useful to summarize the essential points of the proposed mechanism (*4*), before discussing its implications for the electrical properties.

1. Quasi-free electrons act as chemisorp-

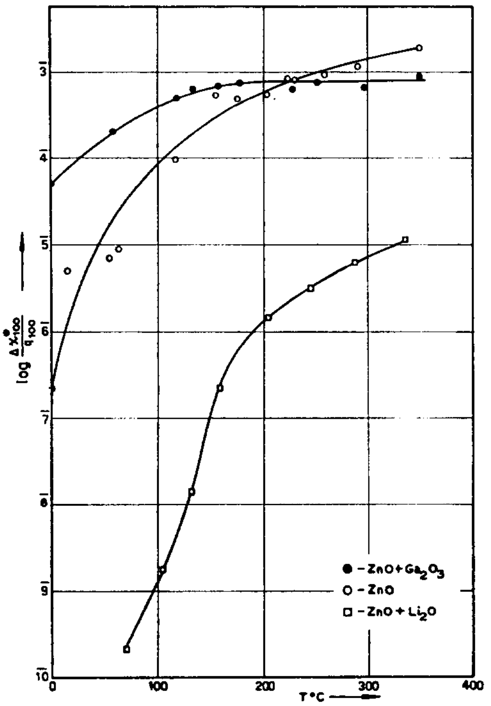

FIG. 13. Average "efficiency" of hydrogen on ZnO, $ZnO + Ga_2O_3$, $ZnO + Li_2O$ samples as a function of temperature (see text).

tion centers, according to the equation $Zn^{2+} + e + \frac{1}{2} H_2 = ZnH^+$. The number of quasi-free electrons initially present at the surface allows a high initial adsorption rate. This number is, however, insufficient to account for the *total* number of chemisorbed atoms (corresponding to about 15% of the total surface area). It follows that sites for adsorption must be created and, in fact, it is shown that the majority of bonds are formed with centers which have been created in the course of the adsorption process. In our treatment, the energy liberated by the exothermic adsorption process is responsible for electron excitation from the valence band, or nearby levels, to the conduction band, or nearby levels (electron traps). Excited electrons can enter into new bonds. They can also recombine with the holes created by the excitation process.

2. Holes, created by the excitation process, can recombine with electrons, or they can be captured in hole traps, or they can lead to different hydrogen to surface bonds: $O^{2-} + p + \frac{1}{2}H_2 = OH^-$. Holes were therefore acting as adsorption centers.

3. The ZnH^+/OH^- ratio depends on the lifetime of electrons and of holes, and also on the sticking probability of hydrogen according to the two different reactions. It can be shown that, according to our mechanism, the parameter α of the Elovich equation, which is a measure of the deceleration of the adsorption process, is given by $\alpha = K/\tau_e \gamma_e n_e P$ for the process utilizing electrons (ZnH^+ formation). Here, n_e is the number of electrons, γ_e is the sticking probability of hydrogen molecules at ZnH^+, τ_e is the lifetime of the electrons, P is the pressure, and K is a constant.

An analogous expression, but with quantities referring to holes, can be derived for the formation of the OH^- bonds. All quantities appearing in the above expressions are functions of both temperature and surface coverage. The functions are not necessarily the same, in the more general case, when electrons and holes are involved. It can therefore be anticipated that the ZnH^+/OH^- ratio will depend on both coverage and temperature.

4. In addition to the forms just described, a third type of hydrogen surface bond will be formed at high temperatures. The OH^- bond can transform into $O^2 + H^+$. The proton is likely to have a higher diffusivity and in this form hydrogen can diffuse into zinc oxide. Diffusivity into the interior can be limited, at low enough temperatures (roughly below 400°C), to the first few layers. A lowering of the Fermi level will favor the formation of the third type of bond.

Influence of temperature. The consequences of chemisorbing hydrogen in different forms can now be considered with respect to the influence on the electrical conductivity of zinc oxide. Since the majority of electrons and holes engaged in bonds derives from the excitation process, the total number of excited electrons must be equal to the total number of holes, as stated in the equation

$$ZnH^+ + n_e + n_T = OH^- + p_T \qquad (1)$$

The left member shows that electrons are distributed among bonds (ZnH^+), conduction band (n_c) and electron traps (n_T). The right member shows that holes are distributed among bonds (OH^-) and hole traps (p_T). No free holes are considered in this equation, since holes are very effectively trapped in zinc oxide. This point is clearly shown by the work of Heiland (*16*) on photoconduction. While photoexcitation leads to an increase of concentration of electrons, the corresponding holes cannot be detected. Thus, holes created in an excitation process are ineffective for electrical conduction.

It can now be understood why the conductivity increase is small at low temperatures, and why it should increase with increasing temperature. At low temperatures, most of the excited electrons are either engaged in ZnH^+ bonds, or trapped by electron traps. As the temperature is raised: (a) the number of trapped electrons will decrease; (b) the number of ZnH^+ bonds will also decrease above a certain temperature, namely around 80°C, as shown by adsorption isobars. Adsorption isobars also show that the second type of hydrogen, identified here with the form OH^-, increases up to about 200°C.

As a consequence the ratio between the number of electrons in the conduction band and the number of holes engaged in a bond increases with temperature.

As a limiting case for high temperature adsorption, one could expect one electron in the conduction band for every hole engaged in a bond. The proposed model of hydrogen chemisorption would therefore account for the observed increase of "efficiency" of the adsorbed hydrogen when temperature is increased. To account for the difference in the efficiency of hydrogen bound as OH^- and O^{2-}—H^+ (third type), one could admit that the two types of bonds correspond to donor centers of a different depth in the forbidden region of the semiconductor (see next section). It can be noted that a hydrogen atom (or ion) can be accommodated into two different interstitial positions of the zinc oxide lattice, with coordinates $(2/3, 1/3, 1/2, +u/2)$ and $0, 0, 1/2, +u/2)$, respectively. These positions are characterized by a different symmetry and different distances with neighboring ions. When the adsorption involves the external layers of the oxide, occupation of different interstitial positions might favor different types of oxygen–hydrogen bonds. An alternative or additional explanation also exists to account for the different efficiency of the high temperature forms, OH^- and O^{2-}—H^+. If the H^+ form diffuses more readily into the interior of the oxide, the accumulation layer (see next section) will be thicker, and the conductivity will be larger.

The dependence of conductivity on the amount of gas adsorbed. An inspection of Figs. 3, 5, 11, and 12 shows that for both pure ZnO, and Ga-doped samples, the efficiency $d\chi/dq$ is not constant.

The dependence of $\Delta\chi$ on q is a function of temperature: at low temperature $d\chi/dq$ increases with surface coverage, while at higher temperature $d\chi/dq$ decreases when q increases. The causes which determine the sign of $d^2\chi/dq^2$ will now be examined.

At low temperature, $d^2\chi/dq^2$ is positive. It immediately follows from Eq. (1) that the number of electrons in the conduction band, n_c, increases with the OH^-/ZnH^+ ratio. As discussed in reference (*4*), at the beginning of the adsorption process the lifetime of excited electrons is larger than the lifetime of the free holes. The formation of ZnH^+ is therefore favored with respect to the formation of OH^- bonds. As coverage increases, the difference between the two lifetimes becomes less marked. Furthermore, the sticking probability leading to ZnH^+ may decrease more than the sticking probability leading to OH^-. It follows from the above considerations that according to our model the OH^-/ZnH^+ ratio increases as the coverage increases. This corresponds to the increase of the efficiency of hydrogen observed by Barry and Klier (*9*) and by us, at low temperatures.

At higher temperatures, $d^2\chi/dq^2$ is negative. This behavior requires a more detailed analysis. Let us visualize the ZnO powder as a stack of cubes each of size d

equal to the average particle size. Each cube will possess a surface "accumulation layer" of depth l. The powder is held between two electrodes of section s placed at a distance h. The total conductivity of the powder is then given by the expression:

$$\chi = (s/h)[4\xi_R(l/d) + \xi_I] \qquad (2)$$

where ξ_R is the specific conductivity of the accumulation layer and ξ_I is the bulk specific conductivity of the oxide. The specific conductivity ξ_R is given by: $\xi_R = \mu_R n_R$ where n_R is the electron concentration in the accumulation layer, and μ_R is the mobility. When $\xi_R \gg \xi_I . n_R$ is given by: $n_R = \nu/l$, where ν is the number of surface positive charges/cm^2; ν is given by the total number of chemisorbed atoms multiplied by the fraction B of donor centers dissociated into one electron + ionized center: $\nu = Bq$. Equation (2) can be written as:

$$\chi = (s/h)[(4/d)\mu_R Bq + \xi_I] \qquad (3)$$

If ξ_I remains constant, differentiation with respect to q gives:

$$d\chi/dq = (4s/hd)\{\mu_R B + q[(d\mu_R/dq)B + (dB/dq)\mu_R]\} \qquad (4)$$

The two functions $B(q)$ and $\mu_R(q)$ will therefore determine the dependence of $\Delta\chi$ on q. $B(q)$ and $\mu_R(q)$ will themselves be determined by the electronic structure of the surface in the presence of ionized surface donors. Under these circumstances the electric field set up by the adions gives rise to a space charge region on the surface ("accumulation" or "enrichment" layer), which penetrates into the interior of the semiconductor to a depth l.

The concentration of the carriers and their mobility within the space charge region are both functions of the potential drop between the surface and the interior of the semiconductor. The potential drop is itself a function of surface coverage. A refinement of the theory of space charge regions created by adsorption has been developed for ZnO by Krusemeyer and Thomas (*13*). According to this treatment the ratio between the number of ionized donors and the total number of donors present on the surface decreases with increasing surface coverage, as the lower edge of the conduction band approaches the Fermi level at the surface. This result is in agreement with the qualitative prediction of Volkenstein (*14*). The treatment also shows that the percentage dissociation of donors is largely determined by the position of the donor level within the forbidden gap of the oxide. While at low coverages the donors are 100% ionized, at saturation the dissociation drops markedly. As an example, the dissociation of donors at surface saturation varies between 6% and 0.1% according to whether the donor level lies at the lower edge of the conduction band, or 0.7 volts below it. With the treatment of Krusemeyer and Thomas it is possible to calculate the function, with the simplifying condition of a zero concentration of surface electron and hole traps.

As for the $\mu_R(q)$ function, Schrieffer has shown (*15*) that in the space charge region, the ratio μ_R/μ_I between the carrier mobility in the layer and the bulk mobility decreases with increasing surface potential.

It is therefore apparent that when the surface coverage increases there is a decrease of the dissociation of donors and of the mobility of carriers within the space charge region. According to Eq. (4), it follows that $d\chi/dq$ should decrease with increasing q.

A simplified treatment of the space charge region, which takes into account the presence of surface traps has been given by Heiland, Mollwo, and Stöckmann (*5*). This treatment enables one to calculate the increase of the number of conduction electrons caused by a given increase in surface donors, if the hypothesis is made of complete donors dissociation. For an accumulation layer, with a trap density S at the Fermi level, the following equation is approximately obeyed:

$$\Delta\nu_c/\Delta\nu = \nu_c/2SkT \qquad (5)$$

where ν_c is the number of conduction electrons/cm^2 in the conduction band. The above equation is valid when $\Delta\nu_c \ll \nu_c$; $\Delta\nu_c \ll \Delta\nu$.

According to this treatment, the efficiency of hydrogen is higher, the higher the initial conductivity (determined by ν_c) and the lower the density of traps. A small efficiency thus corresponds to the fact that the electrons donated to the oxide will mostly be found in electron traps. Only a small fraction of the electrons will therefore contribute to the conductivity in the conduction band. If the trap density were constant, the efficiency should increase with coverage. Measurements of photoconductivity and field effect (*16*) do however indicate an increase of the trap density as the Fermi level approaches the conduction band. Such an increase of trap density can obviously be partly responsible for the observed decrease of the efficiency with increasing coverage.

In summary, it can be said that there are two main factors which determine the dependence of conductivity on the amount of chemisorbed hydrogen. These factors are: (1) The presence of different types of chemisorbed hydrogen. The ratio between the different types is a function of both coverage and temperature. (2) The presence of an accumulation layer. Three distinct reasons can contribute to the decrease in the efficiency as coverage increases: decreasing ionization of donors, decreasing carriers mobility, and increasing traps density.

It can be noted that the $\Delta\chi$ vs. q curves seem to indicate that above about 260°C, $d^2\chi/dq^2$ becomes positive at the highest coverages. This behavior can probably be ascribed to an increasing importance of the ionic chemisorption, O^{2-}—H^+. The ionic bond is likely to be characterized by a higher efficiency, as discussed in the section on Influence of Temperature. The importance of this third type of chemisorption should increase with temperature and with amount of chemisorbed gas.

The influence of pressure. If the increase of conductivity were a single valued function of the chemisorbed amount, one should expect an overlap of $\Delta\chi$ vs. q plots, determined at the same temperature but at different pressures. As shown by Figs. 5 and 12 this is not the case in the system being investigated. It appears that a better overlap is obtained if $\Delta\chi$ is plotted as a function of $(q - q_0)$, as indicated by these figures. The slow chemisorption process to which the $\Delta\chi$ vs. q curves refer is always preceded by a very fast process obeying different kinetics. The results represented by the curves of Figs. 5 and 12 therefore seem to indicate that the efficiency of the hydrogen during the fast initial process depends on q in a way which is different from that observed during the slow process. A better overlapping of the curves is therefore expected if one subtracts from q the contribution q_0 of the initial process. Figure 14 is an illustration of this point. One should not expect, however, a complete overlapping of the curves, except in particular cases ($\Delta\chi_{q=q_0} \ll \Delta\chi_{\text{tot.}}$). In fact the slow process sets in at values of χ_0 and q_0 which differ according to the pressure. The influence of the initial process on the slow process is therefore different at different pressures.

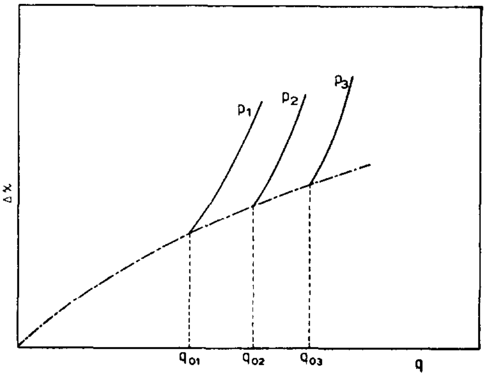

FIG. 14. Schematic representation of conductivity increases caused by: fast initial process (dash-dot line); slow processes at different pressures (full lines).

According to our model of the chemisorption process this behavior is not unexpected. As pointed out in reference (*4*), during the initial stage of chemisorption a stationary state is reached for the two processes of electronic excitation and of adsorption. During this stage the laws which determine the ratios of the different types of chemisorption and their efficiencies can be different from those operating during the stationary conditions of the slow process.

The influence of desorption. It is apparent from Fig. 2 and Fig. 9 that the application of a high vacuum below about 130°C does not markedly alter the value of the conductivity reached during adsorption. The amount of gas desorbed under the same conditions is, however, about 80% of the total. In the temperature region up to 130°C one is then led to the conclusion that the desorption process will mainly involve the hydrogen chemisorbed as ZnH^+, which represents a weaker form of adsorption. The electrons set free when these bonds are broken will recombine in a very short time with trapped holes. As the temperature is increased above 130°C desorption will involve an increasing number of OH^- and of O^{2-}—H^+ bonds. As a consequence the decrease of conductivity under high vacuum will be larger the higher the temperature.

We wish to remark that the value of the conductivity reached after desorption of about 80% of the adsorbed gas does not coincide with the value corresponding to the adsorption of 20% of the gas on an initially bare surface. The ratio of the different forms of chemisorption present at a given coverage does in fact depend on the conditions used to reach that particular coverage. This ratio will be different according to whether a given coverage has been reached by adsorption at different pressures or else by desorption of part of the previously chemisorbed gas.

The influence of the additions of gallium and lithium. The data reported in Fig. 13 give a clear indication that the efficiencies are strongly dependent on the type of addition present in the ZnO lattice. Efficiencies can differ by as much as 6 orders of magnitude at low temperature, while at higher temperatures they become of the same order of magnitude.

The interpretation of these results is complicated by the presence on all samples of three different types of chemisorption. It is, however, apparent from the chemisorption isobars (*2*, *4*) that differences of the above order of magnitude can not be attributed to different ratios between the amounts chemisorbed in the various forms.

The presence of electron traps can explain the observed effects. Conductivity (*5*, *17*) as well as infrared absorption measurements (*18*) have in fact shown the presence of low lying traps in Li-containing samples. According to Eq. (5), the low efficiency of these samples could then be attributed to a very efficient trapping of the electrons by these traps. As the temperature is increased the traps are progressively emptied and the efficiencies on the various samples will therefore merge at high temperature. This interpretation receives further support by the data reported in Figs. 1, 6, and 8. An examination of the curves referring to samples which have adsorbed hydrogen at 400°C, does in fact show that the temperature coefficient of conductivity decreases in the order: ZnO + lithium, ZnO, ZnO + gallium. This observation suggests that when the temperature is lowered the electrons donated to the conduction band at high temperature will progressively fall back into the traps. As a consequence the deeper the traps, the higher will be the temperature coefficient of conductivity.

The above considerations have been based on the assumption that donor centers and electron traps represent discrete energy levels in the forbidden gap of the oxide.

The presence of an impurity band, extending to a certain depth below the conduction band, represents an alternative possibility. The existence of an impurity band in zinc oxide was formerly postulated for crystals with a high concentration of donors (*10*, *19*). More recently G. Bogner (*20*) has interpreted the electrical behavior of ZnO at low temperature on the assumption of the presence of an impurity band even at donor concentration of the order of $10^{17}/cm^3$.

The presence of impurity bands of the type discussed in Bogners' paper does not modify the general considerations which have been developed in the preceding pages. One should obviously take into account in this case the different features of the impurity bands in the various samples.

Surface Reduction and Electrical Conductivity

As mentioned at the beginning of this discussion the positive influence of hydrogen on the electrical conductivity of zinc oxide has been attributed by Thomas and Lander (*10*) to the reducing action of hydrogen.

The surface reduction of the oxide creates new donor centers represented either by the excess zinc formed or by anion vacancies.

This alternative interpretation was put forward on the basis of the following observations: (1) The absorption of zinc vapors on the surface of the oxide causes conductivity changes very similar to those observed when hydrogen is adsorbed. (2) The dependence of the conductivity increase on the hydrogen pressure, at 300°C, shows a marked hysteresis according to whether the measurements are taken at increasing or at decreasing pressures. The later effect corresponds to our observation that the application of a high vacuum following an adsorption experiment does not restore the initial value of the conductivity, unless the sample is heated above 400°C. This observation doesn't necessarily imply a reduction mechanism.

More recently the reduction mechanism has been invoked by Kubokawa (*8*) to interpret new observations.

He determined the kinetic parameters of the adsorption process directly from adsorption experiments and indirectly from conductivity measurements. Use was made in these experiments of a technique consisting in rapidly raising or lowering the temperature or the pressure and in deriving the kinetic parameters by extrapolation at the time of the rapid change.

The results obtained by this method show that the kinetic parameters of the adsorption process, as derived by the direct method, are markedly different from those obtained by conductivity measurements. It was then concluded that the positive action of hydrogen on the conductivity is not related to the adsorption process. Kubokawa attributes the electrical effects to a reduction mechanism. The failure of detecting measurable amounts of water in the desorbed gases seems furthermore to indicate that only a very small fraction of the adsorbed hydrogen is responsible for reduction. The positive effect of hydrogen at low temperature, where the reduction mechanism is less plausible, is attributed to a different cause not specified. A brief comment on these experiments will be given here, while a more detailed analysis will be presented elsewhere. The kinetic parameters of the adsorption process are derived from conductivity measurements on the basis of the following relationship:

$$(dq/dt)_c = (d\chi/dt)_c \cdot (dq/d\chi)_c \qquad (6)$$

The derivatives must be evaluated at the same donor concentration c. If E is the activation energy of adsorption, E_1 the temperature coefficient of the efficiency $d\chi/dq$, and E_2 the temperature coefficient of the conductivity increase $d\chi/dt$, it follows from Eq. (6) that $E = E_2 - E_1$.

The value of E_1 which he determined is about 0.5 kcal. The experimental value of E_2, about 21 kcal, is then practically coincident with E. The value of E determined from adsorption experiments is, on the contrary, of the order of 7–10 kcal.

In contrast with these results of Kubokawa the efficiency determined in our experiments is characterized by a marked dependence on the temperature, on the amount of gas adsorbed and on the conditions used to reach a particular coverage. Values of E calculated from our experiments according to Eq. 6 would therefore be lower than E_2. This should remove one of the objections by Kubokawa. The disagreement between his results and ours can be attributed to the method that he adopted for the determination of E_1. This quantity is obtained from hydrogen desorption measurements in the range 220°–320°C. Hydrogen had been previously adsorbed at 400°C. The surface coverage in desorption measurements is, however, essentially different from that prevailing in the determination of E_2. Values of E_1 determined by this procedure can therefore only be meaningful under the assumption that there is no relationship between chemisorption and conductivity, or else that the efficiency $d\chi/dq$ is independent of both temperature and surface coverage. These assumptions are consistent with the general picture given by Kubokawa. His results, however, can not be taken as proof of the reduction mechanism. The relationships between chemisorption and conductivity outlined in the preceding pages are in fact sufficient to account for the results of Kubokawa. At present all the experimental evidence in favor of the reduction mechanism can also be interpreted on the basis of the direct action of the hydrogen.

It is worthwhile to point out that the essential difference between the two mechanisms consists in the nature of the donor centers created by the interaction of hydrogen with the oxide surface. In fact one can formally speak in both cases of a reduction mechanism. In both cases one can say that only a fraction of the hydrogen is active. It is furthermore apparent from the above discussion, that irrespective of the nature of the donor, the trap distribution is of paramount importance in determining the influence of hydrogen on the electrical conductivity.

The existing ambiguity could only be eliminated if one were able to define the precise nature of the donors by independent experiments. It should be emphasized in this connection that the notation employed in this paper to define the various types of chemisorption (ZnH^+, OH^-, O^{2-}—H^+) represents only a convenient way of describing the formation of bonds with the participation of the electrons or of the holes of the crystal. This notation is not a representation of the actual status of the adsorbed hydrogen. For example, we have seen in the section on temperature influence that the nature of the hydrogen–oxygen bond, is likely to depend on the type of interstitial space occupied by the hydrogen. The possibility also exists that the hydrogen is stretching outwards in a surface OH bond.

A surface OH bond has been identified by Eischens, Pliskin, and Low (*21*) together with a ZnH bond by means of infrared absorption methods. However, they also showed that this surface OH bond cannot be responsible for the conductivity increase. The conductivity increase must be attributed to infrared inactive forms.

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