

Zinc Oxide: An Outstanding Example of a Binary Compound Semiconductor

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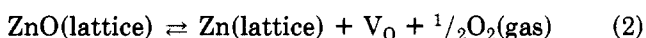
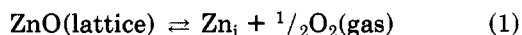
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Zinc oxide is used in a variety of technical applications, including porcelain enamels, heat resisting glass, as an activator in vulcanization, an additive for rubber and plastics, pigment in paints with UV-protective and fungistatic properties, spacecraft protective coatings, a constituent of cigaret filters and healing ointments, semiconductor devices, as a catalyst, in optical waveguides, in piezoelectric materials, and many more. This broad variability is due to the basic properties of zinc oxide, some of which, including its surface properties, are unique.¹⁻⁵

It is well-known that zinc oxide is a n-type broad-gap semiconductor. This was established already in the period 1931-1933 by Jander and Stamm⁶ and Baumbach and Wagner,⁷ and ZnO was one of the first semiconductors extensively investigated. A gap energy E_g of 3.2 eV was obtained from optical measurements at room temperature.¹

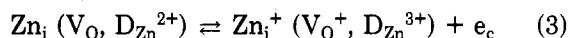
Electronic Properties and Nonstoichiometry

Assuming the hypothetical situation of a perfect and absolutely pure single crystal (no point defects, no impurities, no dislocations, no grain boundaries), ZnO would be an insulator rather than a semiconductor at room temperature. The concentration of "free" electrons in the conduction band would in this case amount to only 4 m^{-3} , compared to 10^{14} - 10^{25} m^{-3} in semiconductors and up to $8 \times 10^{28} \text{ m}^{-3}$ in metals. Real single crystals of ZnO exhibit n-type conductivity with electron concentrations varying over the whole range given for semiconductors, i.e., over more than 10 orders of magnitude. This tremendously large variation in electron concentration is caused mainly by nonstoichiometry of the lattice (metal abundance) and by donor impurities D, both located in the gap below the lower conduction band edge ($\Delta E = 0.025$ - 0.5 eV). This is shown schematically in Figure 1. Nonstoichiometry in zinc oxide is due to native point defects like interstitial zinc (Zn_i) or oxygen vacancies (V_O) which are generated thermally by variation of oxygen (or zinc) pressure and temperature, according to eq 1 or 2. Im-

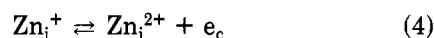


purity donor point defects like Al, In, or other trivalent metal ions can be substitutionally incorporated by a proper doping process (in-diffusion, gas-phase impregnation, coprecipitation, etc.). As native and donor levels are located near the conduction band, they easily can

be ionized thermally, even at room temperature. This process is represented by reaction 3 and increases the



concentration of electrons in the conduction band [e_c] $\equiv n$ appreciably. A concentration of 1 ppm of fully ionized defects generates around 10^{22} electrons/ m^3 in ZnO, giving rise to the possibility of drastically changing the electronic properties in a controlled manner. Because of its availability and low cost of production, ZnO seems like an interesting candidate for cheap electronic components based on p/n junctions. However it has not yet been possible to produce p-type ZnO. The intrinsic contribution (band to band excitation) to the total electron concentration in the conduction band can be important at higher temperatures ($T > 800 \text{ K}$), as it increases with the exponential of the band gap, i.e., $n_i \propto \exp(-E_g/2kT)$. In the range from 800 to 1200 K the increase of n_i with temperature is about 1 order of magnitude for every 100 K. An even more important role is played by the second ionization of native defects, eq 4 and/or the formation of additional donors ac-



ording to eq 1. These properties raise the possibility of using ZnO as a powerful thermistor (negative temperature coefficient (NTC) resistor) and varistor (a resistor whose resistivity changes with voltage).

Photoeffects

Electrons can also be excited by band-gap light ($h\nu = E_g$) from the valence to the conduction band, making ZnO photoconductive. Photoeffects will be especially large if the dark conductivity is very low (nearly insulating). This situation can be achieved for ZnO by appropriate pretreatment of a very pure sample with oxygen at intermediate temperatures or by doping with acceptor impurities such as Li^+ that can substitute for Zn^{2+} ions at normal lattice positions. By these means very pronounced photoeffects can be produced in ZnO, making it a photoconductor of high response. This property is important for electric photocopying, a process for which ZnO is commercially applied. Electrostatic charging is achieved by negative oxygen molecules, O_2^- , from a corona, giving rise to a pronounced space charge layer in the near surface region of the ZnO coating. Surface potentials of 100 V and more occur,

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Wolfgang Hirschwald, born 1930 in Berlin, Germany, took his Diplom at the Free University of Berlin and his Dr. rer. nat. in Chemistry at the Technical University of Berlin. In 1965 he joined the Faculty of the Free University and in 1970 became Professor of Physical Chemistry. His main field of research is the chemistry and physics of compound semiconductors with special emphasis on adsorptive and catalytic properties.

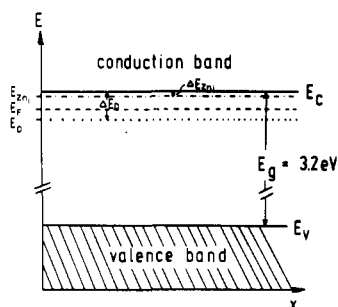


Figure 1. Electronic energy scheme of ZnO (flat band situation) with native (Zn_i) and impurity (D) donors.

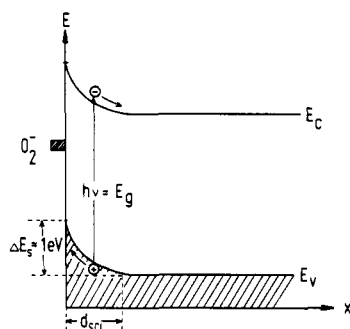


Figure 2. Upward band bending by ionosorbed negatively charged oxygen molecules (O_2^-) and separation of photoinduced pairs by the field across the space charge layer d_{scl} .

giving rise to band bending across a distance of up to 100 nm. The corresponding electrical field ($\approx 10^9$ V/m) effects the separation of electron-hole pairs, generated by band-gap irradiation (eq 5) and prevents their re-



combination (eq 6). The net effect is to maintain a

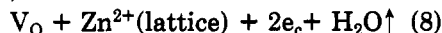
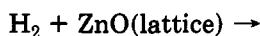


high quantum yield of electrons which contributes to the photocurrent (see Figure 2). The holes which are attracted to the negatively charged surface neutralize adsorbed O_2^- (eq 7), thus discharging those regions of



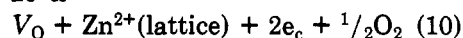
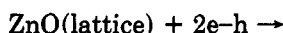
the surface which are hit by photons. If the grains of the photoconductive layer are smaller than 100 nm in diameter, the space charge extends over the whole grain, thus rendering its properties nearly homogeneous.

Nonstoichiometry not only influences the collective electronic properties very strongly but also creates localized active sites at the surface, consisting, for instance, of coordinatively unsaturated zinc ions,⁸ there is an adjacent oxygen vacancy. These sites are obviously active in certain types of catalytic reactions over ZnO, e.g., dehydration. These centers can be generated either by thermal annealing in vacuo, eq 2, or by reduction with CO or hydrogen (eq 8). Another possi-

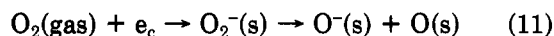


bility is the formation by photolysis of the lattice by

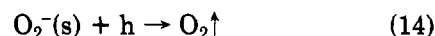
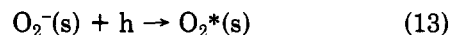
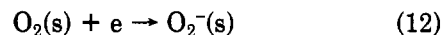
band-gap photons ($h\nu = 3.2$ eV), which has the mechanism shown in eq 9 and 10.



Up to now it has been possible to measure only metal abundance in ZnO. Thus the formation of coordinatively unsaturated lattice oxygen ions by adjacent zinc vacancies is less probable except at ledge or kink positions. On the other hand, oxygen chemisorbs readily as an acceptor on zinc oxide (ionosorption) eq 11, as



established by conductivity, HALL, and ESR studies¹⁰⁻¹⁴ between room temperature and about 700 K. For electrostatic reasons this process of ionosorption is self-limiting, leading to a maximum coverage of 10^{-3} ; i.e., only one in a thousand surface positions is occupied by an oxygen ion. These adsorbed oxygen species constitute localized centers of high activity in catalytic oxidation processes over ZnO. Adsorbed oxygen also influences the photoelectrical and photochemical properties of ZnO as it enhances electronic recombination. This process can yield excited oxygen at the surface $O_2^*(s)$ according to eq 12 and 13 or stimulate desorption according to (14). In general, oxygen plays an important role concerning ZnO behavior, as it influences collective electronic properties, localized active sites, and photochemical behavior as well.



Bulk Structure and Polarity

Bulk electronic properties, optical properties, intrinsic electronic surface states, the ability to become nonstoichiometric, and several other properties of ZnO are governed by the lattice structure and the type of bonding. Zinc oxide forms hexagonal wurtzite-type crystals, crystallizing mostly in the form of needles, with the prism face (10 $\bar{1}$ 0) as the main face, as shown schematically in Figure 3a. The c axis, parallel to the (10 $\bar{1}$ 0) faces, is a polar axis. Cleavage perpendicular to this axis produces the polar faces (0001) and (000 $\bar{1}$), which consist in the ideal case of zinc atoms or oxygen atoms only, as indicated in Figure 3b. The (10 $\bar{1}$ 0) face is in the ideal case a stoichiometric face, i.e., composed of equal numbers of zinc and oxygen atoms. Presuming the existence of the ideal situation, these three stable low index faces offer distinctly different surface sites to any reactants. Different physical and chemical behavior for these three faces is to be expected. This was actually observed with respect to chemical and thermal corrosion^{9a,15,16} and adsorptive behavior.¹⁷⁻²⁰ Chemical

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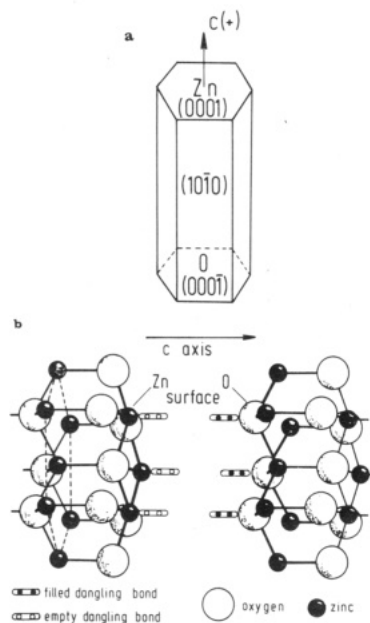


Figure 3. (a) Schematic characterization of the principal faces and anisotropy of ZnO single crystals. (b) Lattice model of ZnO demonstrating the polarity of chemical composition and dangling bonds on (0001) faces (from ref 15).

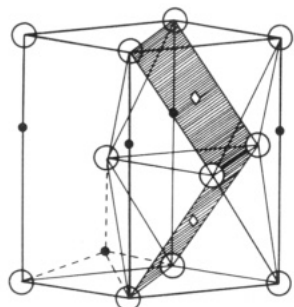


Figure 4. Octahedral interstitial positions forming "channels" in the ZnO lattice (from ref 4): \circ , oxygen; \bullet , zinc; \diamond , interstitial position.

corrosion is much faster for the (000 $\bar{1}$) face compared to (0001), while the opposite is true for the rate of thermal decomposition.

Due to the lattice structure and to markedly different ion radii of zinc and oxygen rather large octahedral interstitial positions exist in ZnO, as shown by Figure 4. Zinc atoms can jump into these positions forming interstitial zinc, Zn_i . The sequence of these octahedral voids form channels in the lattice. This gives rise to a comparatively high diffusivity of zinc in agreement with experimental findings in oxidation studies of thin zinc films.²¹ Interstitial zinc atoms (or monovalent ions Zn_i^+) are probably involved in sintering of ZnO, as this process is much more pronounced for zinc-rich samples if the ambient contains oxygen. In the space charge layer formed by $O_2^-(s)$ or $O^-(s)$, Zn_i^+ becomes highly mobile and migrates toward the negatively charged surface.

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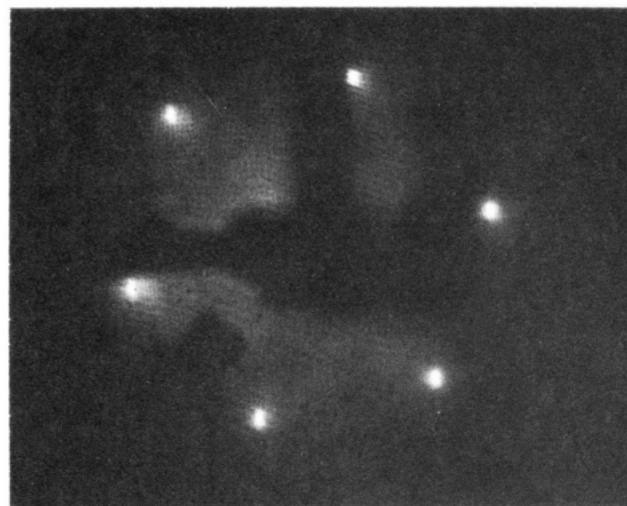


Figure 5. (1 \times 1) LEED pattern of (000 $\bar{1}$) face of ZnO after cleaning as described in the text.

Chemistry and Crystallography of Zinc Oxide Surfaces

Zinc oxide single crystals, grown by chemical vapor deposition, are frequently contaminated by some carbon, sulfur, and chlorine impurities as established by Auger electron spectroscopy. These are surface contaminations which can be easily removed by thermal annealing and slight sputtering with argon ions. After this pretreatment a clear (1 \times 1) structure can be seen by low energy electron diffraction, LEED, as shown in Figure 5. Heating to higher temperatures in ultrahigh vacuum gives rise to a pronounced increase of water desorption, as monitored by mass spectrometry. By annealing at higher temperatures (825 K, 10 min) H_2O can be completely removed. This fact is important since water chemisorbed on a ZnO surface induces Brønsted acid/base equilibria, which play an important role in catalysis. The incorporation of H_2O molecules probably takes place in the course of the crystal growth process, in which hydrogen is involved.²⁰

Polar (0001) and (000 $\bar{1}$) faces can be characterized and distinguished by grazing incidence AES and by low energy ion scattering spectroscopy. With both methods the following oxygen/zinc intensity ratios are obtained.

$$(I_O/I_{Zn})_{(0001)} = 1.0 \quad (I_O/I_{Zn})_{(000\bar{1})} = 1.2$$

Obviously, shielding of zinc ions by the more voluminous oxygen ions is more effective on (000 $\bar{1}$) than on (0001), but not complete.

Chemical reactions on semiconductor surfaces connected with electron transfer can be mediated by electronic surface states. A combination of photoemission yield, surface HALL effect, and work function measurements performed on several single crystal surfaces revealed upward band bending. This indicates occupied intrinsic surface states centered around the Fermi level, i.e., 0.25–0.45 eV below the conduction band edge E_c , with a density of around 10^{15} m^{-2} .^{22,23} Electron energy loss spectroscopy combined with photoelectron spectroscopy led to the conclusion that oxygen-derived occupied dangling bonds and back-bond states with densities ranging from 10^{16} to 10^{19} m^{-2} exist

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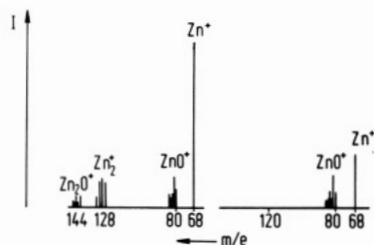


Figure 6. Comparison of secondary ion mass spectra (SIMS) of zinc rich (left) and nearly stoichiometric (right) $(10\bar{1}0)$ faces (from ref 20).

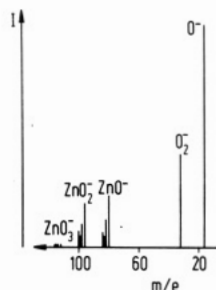


Figure 7. SIMS spectrum of negative ions from $(10\bar{1}0)$ face (from ref 20).

at energies of 2 and 7.5 eV below the upper valence band edge E_v . Empty zinc-derived dangling bond states of similar density are located at about 2 eV above E_c .⁵

Differences in the degree of nonstoichiometry can be monitored by secondary ion mass spectrometry (SIMS). In Figure 6 positive SIMS spectra are given for $(10\bar{1}0)$ faces annealed in oxygen and reducing atmosphere (e.g., H_2 or CO), respectively.²⁰ The reduced sample (zinc rich) exhibits Zn_2 species and a comparatively more

pronounced Zn peak. The spectrum of the negative ions Figure 7 gives evidence to the type of coordination in the ZnO lattice.

Finally, structural disorder, like point defects, kinks, steps, facets, and grain boundaries, strongly influences the reactivity of real surfaces. Thermal annealing in ultrahigh vacuum at 900 K induces formation of oriented steps, as seen by the sixfold splitting of the LEED spots, Figure 8a, and after prolonged times the formation of facets, Figure 8b.²⁰ Indirect evidence for the influence of structural disorder comes from thermal desorption studies performed with CO and ethylene on (0001) faces.¹⁹ Mechanical polishing and chemical etching not only shifts the desorption peaks markedly but also gives rise to desorption of CO_2 (10%) after CO adsorption, whereas from grown or cleaved faces only CO is desorbed.

Summing up, single crystal surfaces exhibit a more complex behavior in ultrahigh vacuum at elevated temperatures than to be expected for a thin polycrystalline layer in a well-defined atmosphere (e.g., oxygen). In the latter system the space charge layer extends across the whole grain and equilibration with the ambient takes place in finite times. Consequently, in experiments described below, thin films of ZnO ($d = 12 \mu m$), consisting of grains of about $0.5 \mu m$ diameter, are studied at $T \geq 400$ K in oxygen atmosphere.

Thermal and Photochemical Reactions of ZnO Surfaces with Oxygen

Thin ZnO films are produced in situ by oxidation of evaporated zinc layers (99.999%) at 625 K under highly clean conditions, i.e., application of purified oxygen (150 mbar) in a vacuum chamber with a liquid-nitrogen trap

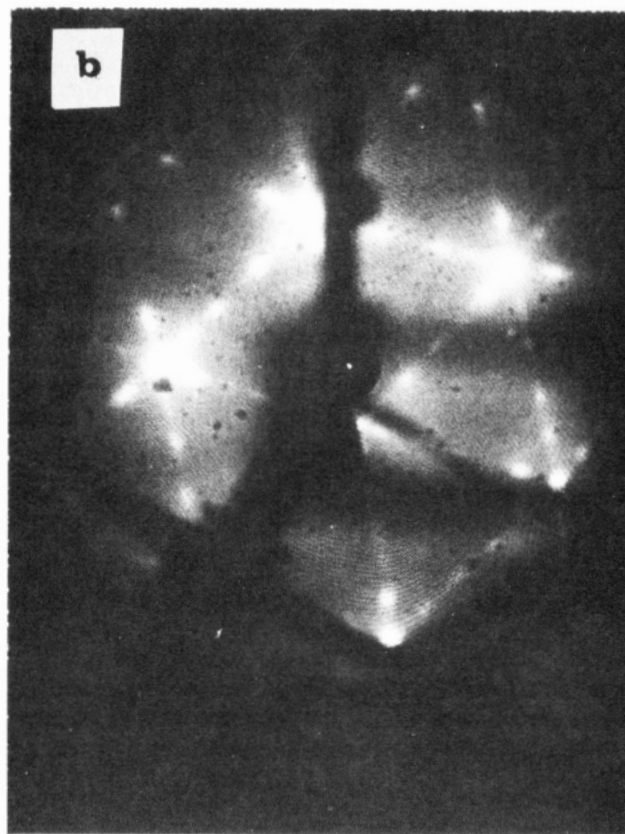
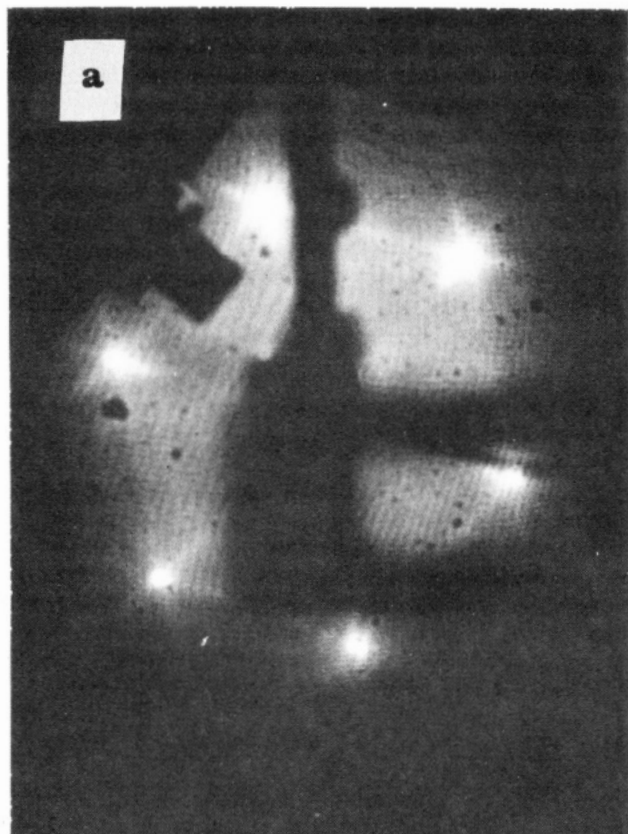


Figure 8. LEED pattern of $(000\bar{1})$ ZnO face revealing step formation (a) and faceting (b) due to thermal annealing in ultrahigh vacuum: (a) 120 min, 900 K; (b) >150 min, 900 K (from ref 20).

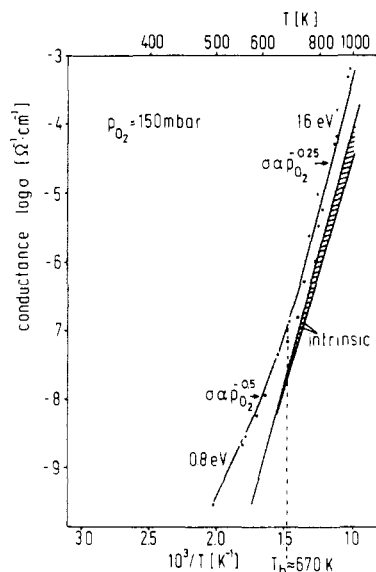
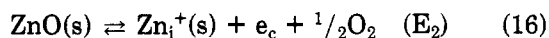
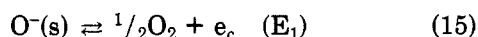


Figure 9. Temperature dependence of conductance in oxygen ($P_{O_2} = 150$ mbar), polycrystalline ZnO layer ($12 \mu\text{m}$ thick):²¹ (—) calculated from eq 17; (●) experimental points.

facing the sample. These measures are taken to avoid any bulk and surface contaminations. Oxidation at 625 K monitored via the conductance of the sample is a fast process, while equilibration of the oxidized but still nonstoichiometric layer is much slower (by a factor of 10^4 at 625 K). Investigations are carried out in a temperature range from 400 to 1000 K and in oxygen atmospheres ranging from 1 to 150 mbar. Changes in temperature or pressure lead to another equilibrium state of nonstoichiometry. These are electrochemical equilibria as the surface is charged under conditions of the experiments. Equilibration times amount up to 100 h at the lower limit of the temperature range. Diffusion of interstitial zinc (Zn_i^+) at these low temperatures is enhanced by the electrical field in the space charge layer, induced by the negatively charged surface, due to adsorbed oxygen ions like $\text{O}_2^-(s)$ and $\text{O}^-(s)$.

Actually, true equilibrium states of ZnO in oxygen below 800 K have not investigated up to now. Results of conductivity measurements are shown in Figure 9. It is known from the work of other authors¹¹⁻¹³ that only $\text{O}^-(s)$ exists above 500 K. Therefore, we have proposed a model (eq 15 and 16) for the low-temperature and



high-temperature region characterized by energy requirements of $E_1 = 0.8$ eV and $E_2 = 1.6$ eV, respectively. In the low-temperature region desorption of ionosorbed oxygen takes place while above 650 K surface donor formation by incongruent vaporization dominates. The dependence of conductivity on temperature and oxygen pressure derived from this model is shown in eq 17.

$$\sigma = \frac{\sigma_0}{1 + (P_{O_2}/P_{O_2}^0)^{1/2}/A_1 \exp(-E_1/kT) + (P_{O_2}/P_{O_2}^0)^{-1/4}A_2 \exp(-E_2/kT)} \quad (17)$$

With the parameters A_1 , A_2 , E_1 , E_2 , and $P_{O_2}^0$ taken from the experiments, this expression is plotted in Figure 9. The calculated curve is in good agreement with the experimental points. Equation 17 also reproduces the

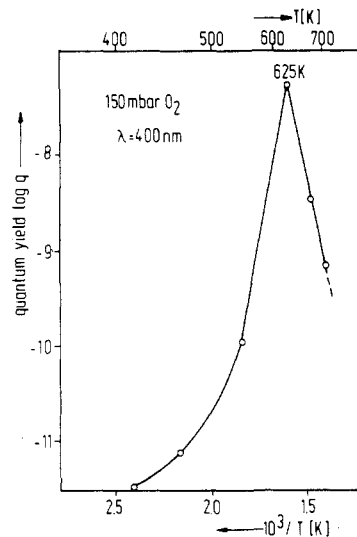


Figure 10. Initial quantum yield q of carrier generation in dependence on temperature at constant oxygen pressure ($P_{O_2} = 150$ mbar).²¹

experimentally observed pressure dependence of the conductivity.²¹

One might be inclined to attribute the high temperature behavior to intrinsic carrier generation ($n_i \propto \exp(-E_g/2kT)$ with $E_g/2 = 1.6$ eV) rather than to thermal donor formation according to eq 16. But the intrinsic carrier concentration also plotted in Figure 10 is too low to be responsible for the high-temperature behavior. Furthermore, thermodynamic calculations of the equilibrium in eq 16 as well as thermochemical studies^{9a} are in good agreement with the experimental energy requirement of 1.6 eV.

If equilibrated samples are exposed for the order of 1 s to band-gap light in an atmosphere of 150 mbar of oxygen, an increase in carrier concentration is always observed. The quantum yield of this process as a function of temperature is plotted in Figure 10. A maximum is observed in the temperature range where the mechanisms change, i.e., where donor generation starts to prevail oxygen desorption. This observation gives further evidence for our model that can be explained in the following way. At low temperatures the degree of coverage is high for oxygen species $\text{O}(s)$ and $\text{O}^-(s)$ which trap electrons, $\text{O}(s) + e \rightarrow \text{O}^-(s)$, and stimulate recombination, $\text{O}^-(s) + h \rightarrow \text{O}(s)$, respectively. In addition, photodesorption can occur according to eq 14. These processes consume part of the photogenerated carriers, thus keeping the quantum yield rather low. With increasing temperature the oxygen coverage decreases effecting an increase in quantum yield. Photodecomposition of the solid may take place according to eq 10 constituting an "irreversible" contribution to charge carrier generation. Removal of negatively charged oxygen species from the surface means, on the other hand, that the electrical field across the space charge layer which effectively contributes to separate electrons and holes decreases with increasing temperature. In the temperature range where donor formation starts to prevail the surface potential will vanish completely. This changed surface situation has two consequences concerning the quantum yield. First, electron-hole pairs are formed in a field-free region effecting a low probability for separation and high rate of recombination, and, secondly, the accumulation of

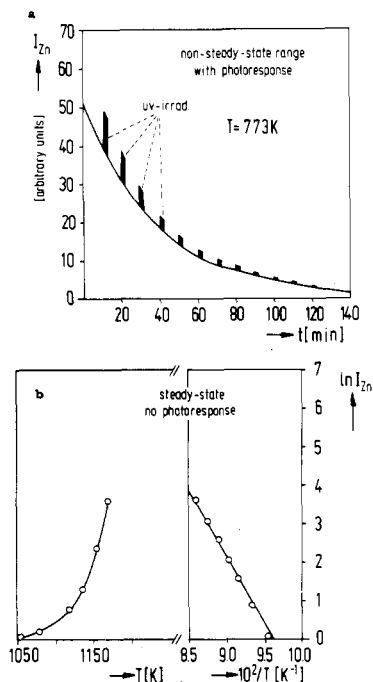
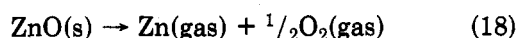


Figure 11. Thermal decomposition and superimposed photo-decomposition of ZnO (polycrystalline and single crystal surfaces exhibit the same behavior): (a) Transient behavior; (b) steady state (from ref 9b).

electrons from thermally and photogenerated ionized donors further increases the probability of recombination. The combined action of both effects will then decrease the quantum yield, in the high-temperature region as observed experimentally.

Thermal decomposition (dissociative sublimation) at higher temperatures (1000–1700 K) was also directly measured by thermogravimetry^{9a,24} and by high-temperature mass spectrometry.^{9b,c,25} These studies reveal dissociative vaporization according to (eq 18). With



fewer than 1% of the ZnO molecules in the gas phase the activation energy of decomposition, E_a , is equal to the band gap ($E_a \approx E_g$). From these experimental observations we infer that the first step of bond breaking in the solid is the excitation of an electron from a bonding state to an antibonding state (valence band \rightarrow conduction band). Actually, it was shown by Hirschwald and Stolze^{9a} that this is the step with the highest energy requirement in the sequence of stepwise dissociative vaporization. If this is true, photodecomposition of the lattice should be possible by irradiation with band-gap light.

Photodecomposition and Intrinsic Stabilization of Zinc Oxide

Experiments carried out in an ultrahigh vacuum mass spectrometric system with a UV lamp attached give direct evidence that photodecomposition actually occurs.^{9b,c,26} In these experiments the zinc intensity was monitored in the gas phase above 600 K (Figure 11). It turns out that photodecomposition is a transient

effect which only occurs on oxygen-annealed surfaces and vanishes after decomposition of about 100 monolayers. This is in agreement with our aforementioned studies of photoconductivity in dependence on temperature: above 625 K the quantum yield decreases by at least 2 orders of magnitude and, even more, after prolonged irradiation. Similar results were obtained at room temperature by other authors.^{27–29} They observed increasing metal abundance, i.e., donor abundance, and quantum yield of photocurrents which decreased by several orders of magnitude with increased time of irradiation. Again, the loss of the field in the space charge layer which attracts holes to the surface and the accumulation of electrons by donor enrichment in the near surface region are responsible for the decay of photoresponse. This becomes clear from the quantitative formulation of photoinduced oxygen release according to reactions a–e, which leave out zinc desorption.

- (a) $2h\nu \rightarrow 2e-h$
 - (b) $\text{O}^{2-}(\text{lattice}) + h \rightarrow \text{O}^-(\text{s})$
 - (c) $\text{O}^-(\text{s}) + h \rightarrow \text{O}(\text{gas})$
 - (d) $\text{O}^-(\text{s}) + e \rightarrow \text{O}^{2-}(\text{lattice})$
 - (e) $\text{Zn}^{2+}(\text{lattice}) + e \rightarrow \text{Zn}^+(\text{s})$
- } photodecomposition
} recombination
} donor formation

From reactions a–e the following rate equation can be derived.

$$\frac{d[\text{O}(\text{gas})]}{dt} = \frac{k_b k_c [h]^2 [\text{O}^{2-}(\text{lattice})]}{k_d [e] + k_c [h]} \quad (19)$$

Equation 19 predicts that oxygen-annealed samples with very low concentrations of electrons ($[e]$) will exhibit a photoresponse proportional to $[h]$, i.e., the light intensity, while reduced, vacuum annealed, or incongruently photodecomposed samples with $[e] \gg [h]$ will show no response to irradiation. Since ZnO is never found to be stoichiometric in equilibrium with the ambient atmosphere, these observations indicate that the ZnO lattice is stabilized toward decomposition by metal abundance at lower temperatures ($T < 1000$ K). Additional, direct evidence to this assumption comes from Göpel's observation that the partial pressure of oxygen over ZnO decreases with increasing metal abundance.³⁰ The corresponding observation for the zinc partial pressure over oxygen-annealed samples is shown in Figure 11a. The percentage of zinc abundance which corresponds to the deviation from stoichiometry increases with temperature, as revealed by the above-mentioned conductivity measurements and also by chemical analysis,⁴ up to a temperature where congruent sublimation starts ($T \geq 1050$ K, according to Figure 11b). Zinc abundance is established by incorporation of zinc atoms in octahedral voids (Figure 4), although at elevated temperatures diffusion of oxygen vacancies from the surface to the bulk cannot be excluded.

The effect of stabilization of the lattice toward decomposition by metal abundance can tentatively be attributed to the simultaneous influence of several effects. High electron densities not only increase the recombination rate of thermally created or photogenerated holes (which correspond to weakened bonds) but

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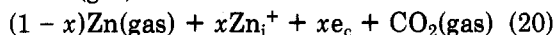
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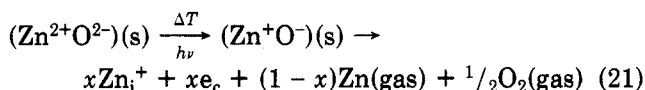
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also reduce the field gradient which is highly effective in pair separation. Furthermore, zinc interstitials Zn_i^+ which correspond to metal abundance can induce an additional Coulombic interaction. A corresponding effect of lattice stabilization is found in chemical surface reactions. For instance, in the course of surface reduction according to eq 20 zinc enrichment as shown

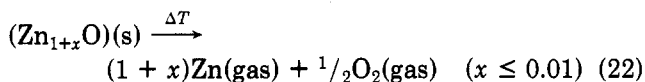


by SIMS studies (Figure 6) and a decrease in surface reduction rate also occur in parallel.³¹ At temperatures above 1050 K zinc desorption highly overrules zinc incorporation into the lattice and thermal decomposition proceeds congruently.

In summary, a low-temperature mechanism is proposed for non-steady-state thermo- or photodecomposition that leads to increased deviation from stoichiometry (eq 21). This response of the system toward



activation by thermal vibrations and photons is shown in Figure 11a. At temperatures above 1050 K the thermal decomposition proceeds according to eq 22. Photoeffects in this range are negligible.



Some Aspects of Catalysis on Zinc Oxide

Zinc oxide is used as a catalyst in hydrogenation and dehydrogenation, dehydration, oxidation, methanol synthesis, and water-gas shift reaction.²⁻⁴ Frequently the activity and selectivity is strongly increased by the addition of metal clusters or oxides of other elements than zinc. For example, a catalyst for low-temperature methanol synthesis consists of a mixture of copper oxide and zinc oxide supported on alumina or chromia.

But even on clean ZnO surfaces there exist specific sites and interesting possibilities for their modification. Neighboring oxygen and zinc ions present, for instance, on (10 $\bar{1}$ 0) faces correspond to adjacent filled and empty dangling bonds which can be regarded as Lewis acid/base pairs. These double sites are especially favorable in adsorbing polar molecules and groups, e.g., OH groups in the course of dehydration of alcohols. Even homonuclear molecules like H₂ can be polarized over these adsorption sites resulting in the formation of OH and ZnH surface groups which were identified by infrared spectroscopy.^{20,32}

On reduced or vacuum-annealed ZnO surfaces these polarizing sites are expected to be present and effective. Indeed, a pronounced activity for dehydration is experimentally observed on ZnO powders pretreated in this way, while oxidized surfaces are inactive in dehydration but active in dehydrogenation.³³ This is an interesting and important aspect concerning the mechanism of methanol synthesis over zinc oxide. This reaction is in practice nearly 100% selective in spite of

the reducing potential of the synthesis gas mixture consisting of CO and H₂. A surface which dehydrates the alcohol to a considerable extent cannot be highly selective as hydrocarbons should also be formed. But the technical catalyst contains copper, as mentioned above. Obviously, copper atoms occupy one site of the center which was active in dehydration. Evidence to this assumption was given by temperature programmed desorption (TPD) of alcohols from clean and copper-covered ZnO surfaces³⁴ demonstrating the suppression of dehydration on copper-covered ZnO surfaces.

Dehydrating centers are "poisoned" not only by copper or oxygen adsorption but also by CO₂. If carbon dioxide is used instead of CO as a reactant for methanol synthesis over pure ZnO, high selectivity for methanol is again established.³⁵ Obviously two channels exist for methanol synthesis over ZnO, and it depends on the state of the surface (oxidized or reduced) which one is preferred.

So far, only the ideal stoichiometric (10 $\bar{1}$ 0) surface has been considered. Taking into account the tendency of ZnO to become more stable by enhanced deviation from stoichiometry, the formation of oxygen vacancies and zinc interstitials at the surface has to be considered after reducing or vacuum pretreatment. Such point defects also constitute polarizing binary centers which can be created on any kind of face. Adsorption of oxygen-containing species on an oxygen vacancy gives rise to a marked interaction and can even lead to abstraction of oxygen. This obviously occurs in dehydration of alcohols or in reoxidation of the surface by carbon dioxide.

Concluding Remarks

Combination of band structure considerations with an atomistic approach, taking point defects into account, leads to an understanding of the behavior and of the properties of zinc oxide. The main stable faces (0001), (000 $\bar{1}$), and (10 $\bar{1}$ 0) consist of distinctly different sites with mainly acid or mainly basic or mixed character. This is the reason for the amphoteric behavior of ZnO and partly explains its unique adsorptive and catalytic properties. In addition, the tendency to become nonstoichiometric and to form interstitials and surface anion vacancies strongly influences the electronic behavior, the thermal stability, and the photochemical and catalytic properties.

New features of transient thermal and photochemical instability have been revealed experimentally. The final state corresponds to lattice stabilization by nonstoichiometry.

The experimentally observed quantum yield of photocurrents and photodecomposition and the maximum of photoresponse at intermediate temperatures can be interpreted in accordance with this behavior.

The description of the solid and its surface presented here turns out to be meaningful for the understanding of some selected aspects of catalysis on ZnO surfaces.³⁶

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