PHOTODESORPTION: A CRITICAL REVIEW

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ABSTRACT

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A critical review of the literature in the field of photo-desorption is presented. Material is covered through December 1975. Although it is impossible to include every paper ever published which is in some way related to photodesorption, we feel that the material covered is sufficiently complete to permit reasonable conclusions to be reached. The literature naturally falls into two basic categories, namely, papers involved with metal substrates and those involved with semiconductor substrates. Since the effects on these two kinds of surfaces are very different, they are each considered in separate sections.

Photodesorption from metals seems to be an extremely inefficient process if it occurs at all. That is, cross sections are equal to or less than 10^{-23} cm^2 . The reason for this extremely low cross section is not yet well understood. Photodesorption from semiconductors seems to be a very efficient process with cross sections as high as 10^{-17} cm^2 . On most substrates studied, eg. ZnO , TiO_2 , CdS , the chrome oxide surface of stainless steel, etc., impurity carbon atoms play a very significant role. On all these

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materials, the single or dominant process involves chemisorption of molecular oxygen onto the impurity carbon surface atoms. Electrons are captured from the conduction band to produce a chemisorbed CO_2^- complex. The application of band gap and higher energy radiation produces electron-hole pairs. Some of the photo-generated holes migrate to the surface where they combine with the negative ion complex. The resulting physisorbed CO_2 is then thermally desorbed. Virtually all of the data in the literature tend to support this model. Following the analysis of the literature, a discussion of additional work to be done as it would relate to the CTR program is presented in the conclusion section.

The reference lists have been separated into two groups, one for metals and one for semiconductors. Each group starts with number 1 and lists all the papers in that group in strict chronological order. This procedure was adopted so that new papers, as they appeared, could be added to the appropriate list, enabling us to establish updated lists in proper order.

PHOTODESORPTION A CRITICAL REVIEW

I. Introduction

The literature in photodesorption can be conveniently divided into two major groups. One group of papers involves descriptions of attempts to measure photodesorption from metal surfaces. The second group describes attempts to measure photodesorption from semiconductors and insulator surfaces. It is now clear that the processes on metals vs. those on semiconductor surfaces is very different. We will, therefore, discuss all the papers on photodesorption from metals separately since they relate to each other and not to the data from semiconductors. Similarly, the papers dealing with photodesorption from semiconductors will be grouped and discussed as they relate to each other.

It should be noted that a number of papers contain the word photodesorption in the title, and yet are not really related to true photodesorption processes. (By true photodesorption we mean a quantum effect whereby a single photon, through a single or multi-step process, causes the desorption of an atom or molecule.) In many cases, for example, results due to radiation induced thermal effects are listed as photodesorption and we will try to indicate which of the experiments we believe fall into this type of category.

We have listed the papers dealing with attempts at measuring photodesorption from metals in chronological order in the biblio-

graphy¹⁻¹⁸. It turns out that this total list can be divided into three or four groups within which papers relate to each other. Therefore, rather than discuss the papers in strict chronological order, we will consider groups of papers which generally relate to each other and form a coherent unit, while following an approximate chronological order.

We have listed the papers dealing directly or indirectly with photodesorption from semiconductors in chronological order in the bibliography, Refs. 1-45, at the end of the review portion of the semiconductor material. This much larger number of papers dealing with a wider area of subject matter will be subdivided into a number of groups, the details of which will be explained in the beginning of the section on photodesorption from semiconductors.

II. Photodesorption From Metals

The first paper describing attempts at measuring photodesorption from metals is that of Lange and Riemersma¹. The system they studied was CO on nickel. (It will be seen that a number of experimenters in later years chose the same system for comparison purposes.) This first experiment, which appeared in print in 1961, was clearly a preliminary, rather limited effort. In this work, only total pressures were measured and the wavelength range covered was from 2800 Å to 5000 Å. The total gas desorbed was extremely

small, resulting in limited signal-to-noise data. The authors were convinced that they were observing true photodesorption and not bulk heating effects, although the justification for this conclusion is not totally convincing. They obtained a maximum photodesorption signal of about 10^{-8} molecules/photon at about 2800 Å. The important data from this paper is shown in Fig. 1. The authors point out that there is considerable uncertainty in interpretation of these tentative results and indicate intention to continue and refine the experiments.

In 1965, two more papers appeared, a second one by Lange,³ and a paper by Adams and Donaldson². Lange's paper indicated a continuation of his earlier experiments with the improvement of mass spectrometer analysis. In this work he still used CO as the backfill gas, but now tried other substrates such as tungsten, pyrex and quartz. In general, he found that maximum quantum efficiencies were always in the order of 10^{-8} molecules/photon or less. These quantum efficiencies always leave one working near the limit of detection capability. The net result of Lange's work was that photodesorption from metals and some insulators was an extremely inefficient process at best.

The work by Adams and Donaldson also concentrated on the study of CO on metal surfaces. In this work only total pressures were measured with an ionization gauge and maximum quantum efficiencies of 10^{-6} molecules/photon are indicated. (In a recent, personal letter from Donaldson, it is indicated that an error was made in labeling the curves and the maximum efficiencies

should appear as 10^{-7} molecules/photon.) Considering the uncertainties in these preliminary experiments, these results can be considered to be essentially the same as those obtained by Lange. It is interesting to note that Adams and Donaldson seemed to detect photodesorption from iron, nickel and zirconium, surfaces which readily oxidize to perhaps semiconductor type materials while they could not detect photodesorption from tungsten or molybdenum surfaces which can be much more thoroughly cleaned. The data of interest in this paper can be seen in Figs. 2 & 3.

In 1971, two short notes appeared relating to photodesorption measurements. One by Peavey and Lichtman⁷ described attempts to measure photodesorption from tungsten using synchrotron radiation provided by the electron storage ring of the Physical Sciences Laboratory of the University of Wisconsin at Stoughton, Wisconsin. The main purpose of their experiment was to try to detect photon induced ion desorption. In this regard, the results were completely negative and only neutral desorption was detected, primarily CO_2 . No quantitative cross section numbers were obtained, but clear cut verification of true quantum photodesorption was available. A typical curve showing the type of data obtained is seen in Fig. 4.

In the other note, Genequand⁶ described the study of CO on evaporated nickel films. Again, two significant features are repeated. One is that the photodesorbed signal detected is primarily CO_2 and secondly, the maximum desorption efficiency (at about 2500 Å) is about 10^{-9} molecules/photon, see Fig. 5.

In 1972, further experiments attempting to observe photo-desorption are reported by Kronauer and Menzel⁸. Here again, they study the system of CO on tungsten. The net result of their experiments leads to an observation of a maximum efficiency of a few times 10^{-7} molecules/photon (corresponding to a maximum cross section of $\sim 5 \times 10^{-21} \text{ cm}^2$) at about $2800 \text{ \AA}$, see Fig. 6. The generalized results are similar to those obtained by the previous workers with the exception of a somewhat higher maximum efficiency. (Also note that Donaldson detected no photodesorption from tungsten surfaces.) This particular paper contains a fairly lengthy review of previous work. There is also considerable discussion of possible mechanisms explaining the data in which it is generally assumed that the photodesorption is similar to electron induced desorption for the same energy range.

During this same year a rather lengthy detailed paper by Paigne⁹ appeared (in French). Once again the system studied is CO on nickel. In this work, considerable care was taken in regard to thermal effects as well as the effect of angle of incidence of the incoming radiation. The final results indicate no effect of angle of incidence and, after subtracting out what he considers to be thermal effects, arrives at a maximum photodesorption rate of 10^{-9} molecules/photon. This value leads him to specify a photo-desorption cross section of less than 10^{-23} cm^2 . The significant data is seen in Fig. 7. These experiments appear to have been done rather carefully with reasonable attention to detail. The values obtained indicated what may be realistic upper limits for

the photodesorption process on metals.

Finally, in 1973, one more detailed study of the CO/nickel system was reported by McAllister and White¹⁰. This paper describes what seems to be the best attempt to eliminate thermal effects. They found a quantum efficiency of the order of 10^{-8} to 10^{-9} molecules/photon but claim that this can be completely accounted for by thermal effects, that is, they can obtain essentially identical results using radiation and direct electrical current heating. (See Figs. 8 & 9) Their analysis seems proper and valid. Unfortunately, their experiments involve radiation of 3200 Å and above and previous results show perhaps considerable effects below this wavelength value. However, there is definite overlap with other work and their conclusions are pertinent.

The net result of all the publications from Lange and Riemersma to McAllister and White lead to the conclusion that for CO on nickel, and perhaps other gases on the same or other metals, the quantum efficiency for true photodesorption is, at best, 10^{-8} - 10^{-9} molecules/photon, perhaps much less and perhaps even zero. This quantum efficiency translates to a maximum cross section of the order of 10^{-23} cm² and perhaps much less than that.

At this point it is interesting to compare these results with the data in a paper published in 1973 by Lee, et al¹³, concerning the absorption cross section values for UV radiation of various gas phase molecules like CO, O₂, N₂, etc. In this paper maximum cross section values of approximately 10^{-17} cm² are measured. See for example, Fig. 10. [Although the wavelength range here is

200-700Å, (the transitions studied require those photon energies), the cross section values obtained are probably similar to those for general gas phase absorption processes.] Thus, photodesorption cross sections for gases on metals are at least a factor of 10^6 less than gas phase absorption cross sections. This seems to indicate that UV photons arriving at a gas covered metallic surface ignore the gas molecules and interact directly with the metal. The energy then seems to be absorbed and distributed with minimal or no contribution to photodesorption.

Based on the apparently minimal, or even absent, photodesorption from gas covered metallic substrates, and the general observation of considerable photodesorption from the walls of stainless steel vacuum systems, Fabel, Cox and Lichtman¹¹ reported on a detailed study of photodesorption from stainless steel. Using very low power densities, in order to completely eliminate thermal effects, they found reproducible efficient photodesorption from stainless steel with a quantum efficiency greater than 10^{-3} molecules/photon, and a threshold for photodesorption of about 2500 Å. (See Fig. 11.) In considering the reason for the exceptional difference in the results obtained on stainless steel as opposed to pure metals, these authors concluded that the difference was related to the fact that the surface of stainless steel is basically a form of chromium oxide, a well known semiconductor. Thus, the implications seem to be that photodesorption can occur from gas

covered semiconductor substrates with relatively high efficiencies but the process is exceedingly less efficient or perhaps even absent on pure metallic substrates. (Further reports from this group describe additional experiments on well established semiconductor substrates and will be discussed in detail in the section on photodesorption from semiconductors.)

The results obtained on the stainless steel can now perhaps help explain some of the observations reported in previous papers. Thus, the reflection of even a very small fraction of incident radiation from the main sample, which might then strike stainless steel walls, etc. could result in an apparent photodesorption signal. The magnitude of this signal would depend on each specific system and could account for the variations reported. Thus, it is interesting to compare the data in Fig. 11 for stainless steel with, for example, the data of Adams and Donaldson² for the CO-Zirconium system, Fig. 3, and the data of Genequand⁶ for the CO-nickel system, Fig. 5. Note the similarity of threshold wavelength. It is also very likely that stray and/or scattered radiation striking the stainless steel walls of the vacuum chamber contributed considerably if not completely to the results reported by Peavey and Lichtman⁷. In addition, those who utilized radiation at wavelengths greater than $\sim 2500 \text{ \AA}$, would not have been bothered by anomalous effects from stainless steel chamber walls. For example, McAllister and White¹⁰ used wavelengths of $3200 \text{ \AA}$ and above and reported no

detectable photodesorption. Thus, in general, contributions from stainless steel surfaces must be considered when interpreting photodesorption data.

During this time interval, a number of papers appeared which seemed to be related to photodesorption, but turned out to be of limited, peripheral interest. The first of these is a paper by Sternberg⁴ in 1966 entitled "A Study of Photodesorption". This paper describes the application of high energy density pulses of radiation sufficient to cause vaporization of copper atoms from solid copper samples. The process here is clearly thermal although the author claims the opposite. The determination of surface temperatures, especially during short (microsecond) high energy (kilowatts) radiation pulses is clearly difficult and not well understood. Since then, of course, many similar thermal desorption processes have been caused and studied, using laser beams.

In 1969, a paper by Moesta and Beuer⁵ seemed to be related to photodesorption. The paper is a short letter to the editor, and discussed apparent changes in contact potential induced by UV radiation on CO covered nickel films. The data and results claimed (eg. quantum efficiencies of about one) seem completely unrealistic and it is difficult to understand what they have actually observed, especially since so much other work has been done on the CO-nickel system with apparently entirely different results. Thus, this paper contributes no useful information to the photodesorption process.

In 1973, a short note by Suzuki¹² appeared. This note dis-

cussed anomalous current-voltage characteristics of a high voltage discharge tube under extreme UV radiation conditions. No quantitative data is presented and it seems much more likely that the anomalous results are due to photoemission processes rather than photodesorption.

Finally, in 1974, a short note by Sowell, et al.¹⁴ appeared discussing the fact that one could produce cleaning effects on metals and ceramic when these materials were exposed to ultraviolet radiation while at atmospheric pressures. Ultraviolet photon reactions with surface contaminants, especially hydrocarbons, undoubtedly do occur. This report is related primarily to the macroscopic cleaning process and, therefore, provides little information to help in understanding photodesorption.

In 1974 and 1975, two papers by Lichtman^{15,16} and one by Menzel¹⁷ appeared, all of which were basically simple review papers, and provided no new information as regards photodesorption.

Finally, in 1975, there appeared a paper by Gersten, et al.¹⁸ entitled "Theory of Photodesorption". The authors, unfortunately, considered only some of the early concepts and assumed that photodesorption was essentially similar to electron induced desorption. Since it is well accepted that electron induced desorption involves direct interaction of the electron with the adsorbed gas molecule, these authors assumed a model involving direct interaction of the incoming photon with the adsorbed molecule. Since careful evaluation of experimental data indicates that the photodesorption process

is clearly quite different than EID, the model taken by these authors cannot lead to useful solutions. Thus, the results they obtained are not particularly helpful in trying to understand and explain the photodesorption process.

At this date one might, therefore, reach the following conclusions. As far as the quantum process of photodesorption of gases adsorbed on metal substrates is concerned, based on a limited number of systems studied, the quantum efficiency seems to be less than 10^{-8} molecules/photon (corresponding to cross sections less than 10^{-22} cm^2) and perhaps much less, even approaching zero. Since gas phase absorption cross sections are very much higher than this, the reason for the very low cross section for photodesorption is not trivially obvious. Some good theoretical work is needed to fully explain this observation. Since photodesorption does occur from semiconductor substrates with rather high cross sections, one must be careful in interpretation of apparent photodesorption data from metal substrates. Thus, scattered light from pure metallic substrates might strike metal oxide surfaces from which photodesorption can readily occur. Stainless steel is an excellent example of an apparent metal whose surface is of a semiconducting nature (chrome oxide) such that very efficient photodesorption occurs from it. Many other metal oxides are good semiconductors and one can detect photodesorption from them. Some well known examples include zinc oxide, TiO_2 , etc. A real understanding of the photodesorption process must, therefore, come through careful studies of semiconductor surfaces.

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PHOTODESORPTION - Figure Captions - Metals

- Fig. 1: Wavelength dependence of photodesorption of CO from nickel. From the work of Lange and Riemersma. (Adapted from Ref. 1)
- Fig. 2: Desorption efficiency from the CO-Ni system. Taken from the work of Adams and Donaldson. (Adapted from Ref. 2)
- Fig. 3: Desorption efficiency for the CO-Zr system. Taken from the work of Adams and Donaldson. (Adapted from Ref. 1)
- Fig. 4: Photodesorption of CO₂ using non-monochromated synchrotron radiation. Taken from the work of Peavey and Lichtman. (Adapted from Ref. 7)
- Fig. 5: Photodesorption efficiency for the CO₂-CO/Ni system. Taken from the work of Genequand. The $m=28$ and $m=16$ data are clearly fragment patterns of the CO₂(44) signal, a fact the author seems to have missed. (Adapted from Ref. 6)
- Fig. 6: Photodesorption probability of CO from W as a function of wavelength. Taken from the work of Kronauer and Menzel. (Adapted from Ref. 8)
- Fig. 7: Photodesorption as a function of wavelength for the CO-Ni system. Taken from the work of Paigné. (Adapted from Ref. 9)
- Fig. 8: Data comparing apparent photodesorption with true thermal effects for the CO-Ni system. ● 3200 Å radiation
▲ electrical current. Taken from the work of McAllister and White. (Adapted from Ref. 10)
- Fig. 9: Comparison of apparent photodesorption with true thermal effects for the CO-Ni system. ● 3200 Å radiation
▲ electrical current. Taken from the work of McAllister and White. (Adapted from Ref. 10)
- Fig.10: Absorption cross section of carbon monoxide gas for a range of UV radiation. Taken from the work of L. C. Lee, et al. (Adapted from Ref. 13)

Fig.11: Photodesorption efficiency as a function of wavelength from a 304 stainless steel surface. Note order of magnitude of the ordinate as compared to previous curves. Taken from the work of Fabel, Cox and Lichtman. (Adapted from Ref. 11)

FIG. 1

FIG. 2

FIG. 3

Relative Signal

FIG. 4

FIG. 5

FIG. 7

FIG. 8

FIG. 9

FIG. 10

FIG. 11

III. Photodesorption From Semiconductors

The material to be covered in this section starts with papers from the 1950's and involves a rather wide variety of topics. To consider the papers in strict chronological order would lead to a rather erratic discussion. Therefore, this section will consider the papers in chronological order within six specific categories. These categories, or groups of papers, include:

- 1) papers describing initial work in the 1950's
- 2) papers which describe specific measurements on photodesorption
- 3) papers which provide useful information on photodesorption, although measurements are limited to surface conductivity and/or chemisorption.
- 4) papers involving other experimental techniques
- 5) papers of peripheral interest
- 6) review papers which contain information relevant to photodesorption.

After these six categories are covered, we will attempt to summarize the overall conclusions that seem valid at this time.

1. A discussion of the initial work may well start with the chapter by R. Morrison³ which appeared in Advances in Catalysis in 1955. This was, to a certain extent, a review paper and was concerned primarily with adsorption. The significant comments in

this paper are related to the realization and verification that surface conditions strongly affect conductivity measurements on ZnO. Although Morrison did not discuss photodesorption per se, he did note that both Heiland¹ and Melnick² had found conductivity changes after UV illumination of ZnO samples which then required oxygen ambients to allow for reversible behavior.

Melnick continued his studies on the surface conductivity of ZnO⁴. He reported results on samples of sintered ZnO powder, considering basically surface conductivity changes under illumination and the effect of ambient oxygen pressure. Although he made no specific photodesorption measurements, he did propose a model which involved the recombination of a photogenerated hole with an O_2^- chemisorbed ion leading to the desorption of oxygen. In the following year (1958), the first qualitative paper on photodesorption from ZnO was published by Medved⁵. After reviewing Morrison's chemisorption model and Melnick's prediction of photodesorption, Medved proceeded with qualitative calculations of the predicted effect of photodesorption on the pressure in his system. His experiments were done on ZnO pellets in a moderate vacuum system (pressure approximately 10^{-6} Torr). Medved did observe photo-induced gas release which he assumed was oxygen. Careful evaluation of his data indicates that changes in pressure in his system under illumination were not well-correlated with accompanying changes in surface conductance. Fig. 12 shows some of his results and it seems rather likely that his observations

were related primarily to thermal desorption.

That same year another report on photo-induced surface conductivity appeared relating to measurements on single crystals of ZnO. This work, by Collins and Thomas⁶, did not measure photodesorption directly; however, the model of holes, produced by band gap radiation, combining with oxygen ions at the surface was again proposed and correlated to their conductivity measurements.

This initial group of papers, describing work done mostly on ZnO surfaces, led, by the late 1950's, to the following status of the view of photodesorption from semiconductors. Photodesorption requires band gap radiation, therefore, the process probably involves photo-generated electron-hole pairs. The model then considers that the holes, migrating to the surface, can recombine with negatively ionized chemisorbed species. (This aspect is strongly supported by observed conductivity changes.) With the chemisorption bond broken, the surface adsorbed species are then considered to desorb. Since it was found that an oxygen atmosphere was necessary to produce the reverse change in conductivity, it was assumed that oxygen was the photodesorbing species.

2. In this subsection we will discuss, in chronological order, those papers which describe specific measurements on photodesorption. Although Medved's paper⁵ describes an attempt to measure photodesorption, his results, as mentioned above, appear to have been due

primarily to thermal processes. We will, therefore, start this subsection with the paper of Fujita and Kwan⁸ which appeared in 1959. This early work was rather limited by the use of vacuum working pressures in the range of 10^{-2} to 10^{-4} Torr. Photodesorption from ZnO powder samples was detected by total pressure measurements only. Although the experimental conditions were far from ideal, they apparently did observe true photodesorption. A typical result is shown in Fig. 13. Since they only measured total pressure, there is no specific information on the desorbing species, (which the authors once again assumed to be oxygen). Of significance is the fact that they observed photodesorption only after exposure of the sample to oxygen, that is, they found no effect with other gases such as helium, hydrogen, nitrogen, CO, CO₂ and H₂O. Since their results were quite limited, their discussion concerning mechanisms was rather vague.

The next description of photodesorption measurements is found in a paper by Haber and Stone¹² in 1963. This work was done on NiO semiconductor surfaces. Unfortunately, the experiments were again done at relatively high pressures (the order of 10^{-2} Torr) so that only total pressure changes were detected. They studied only oxygen covered NiO surfaces, considering the adsorption of oxygen as a major part of the work. They claimed that photodesorption was confined to the wavelength range of 600-900 nm and the amount of photodesorption was found to exponentially decrease with illumination time. A major part of the paper is devoted

to an attempt to explain the experimental data using crystal field theory. Thus, the photodesorption mechanism is linked to the d-d transition in Ni^{+3} ions. Since we are unaware of any further progress with this system or this theory it is difficult to evaluate its validity. The theory does not seem to be one that is related to the photodesorption process in other materials so that this paper does not contribute significantly to our general understanding of photodesorption.

In 1969, another paper on photodesorption was published by Lisachenko and Vilesov²⁶. This rather short report described what appears to be a proper mass analysis (using a time-of-flight mass spectrometer) of true photodesorption from a powdered ZnO sample saturated with water vapor. The paper describes some experimental results, the main points being the verification of the specific quantum interaction of light with the adsorbed molecule and the desorption of OH radicals. Unfortunately, no data curves are provided and there is virtually no discussion of mechanisms. However, two comments in the paper should be noted. One is the statement "The search for photodesorption of oxygen on oxidized specimens yielded negative results". The second statement is "On illumination of a CO/ZnO system, (the ZnO has been previously saturated with oxygen) it is CO_2 rather than CO which is liberated into the gas phase." Both of these statements will prove to be significant as we discuss later papers. Although the results in this paper were promising, the scope of the work was apparently not pursued in any depth. The main interest was in detecting the photodesorption of OH radicals from the water vapor saturated sample. It is

unfortunate that they did not follow up on the photodesorption of CO_2 .

In 1971, there appeared an interesting paper by Baidyaroy, Bottoms and Mark³⁰ concerning the study of photodesorption from powdered CdS samples. In this paper both mass analysis and the spectral dependence of photodesorption were included. The basic observations again verified the requirements of band gap radiation to produce photodesorption. They observed, primarily, photodesorption of CO_2 . (They also detected small increases at m/e values of 14, 32, 34, 40, 44 and 46.) Unfortunately, as with the previous work, they neglected to follow up on the CO_2 observation, assuming it was not related to the true photodesorption process.

The following year a paper appeared by Greenberg³⁴ which considered photodesorption from interstellar dust grains. The motivation for this work was clearly quite different from all previous efforts and was related to concern about the mechanism of molecular development in interstellar space. Measurements were made with a large variety of gases on quartz substrates. In this work only an ion gauge was used to detect changes in total pressure. The conclusion of the author was that photons interact directly with adsorbed molecules. It is difficult to evaluate this work since no graphs or figures were given. There seems to have been no follow up on this work since we have seen no other references from this author or laboratory since this one paper appeared. These factors, and the fact that they used neither mass analysis

nor detailed wavelength dependence, makes it difficult to ascertain the significance of their quantum yield values of up to 10^{-5} mol/photon.

In 1974, we find another paper from the group of Vilesov et al.³⁷. In this work they were still using time-of-flight analysis and were considering the system NO on Al_2O_3 . Again, the experiment seems to have been fairly well done and it appears that they did observe true photodesorption of NO from the α - Al_2O_3 sample. They found a threshold at 230 nm (5.4 eV), which seems quite reasonable as a band gap value. The main purpose of this work was to determine the kinetic energy distribution of the photodesorbed products. Their results indicated that the emitted molecules were photodesorbed with a thermal energy distribution. This fact is probably the most important aspect of that particular paper since it verifies the concept that the neutralized physisorbed surface specie is thermally desorbed.

A paper appearing in 1974 by Petrera, Trifiro and Benedek⁴⁰ considered the photodesorption of oxygen from SnO_2 and TiO_2 . Unfortunately, measurements were done under relatively poor vacuum conditions, i.e. 10^{-1} to 10^{-4} Torr. Therefore, only total pressure measurements were taken using a Pirani gauge. The light source was a 150 watt lamp and no attempt was made to filter the source in any way to provide wavelength data. They measured total pressure changes assuming all increases and decreases were due exclusively to oxygen adsorption or desorption. The net result of all this

limited experimental technique was that no quantitative data useful to our study could be extracted from it. Their phenomenological model, which is based on assumptions which we now know are incorrect, is, therefore, also of no particular value.

Also in 1974, we found a paper by Steinbach and Harborth⁴³ which was concerned with reactions, including photodesorption, on single crystal ZnO. At first, this appeared to be a very good experimental report. Careful reading, however, revealed the following problems. All experiments were done with the sample at a base temperature of at least 400C. (It is known that this is close to the onset temperature for detectable sublimation of ZnO⁴².) The light source used was a 500 or 1000 watt arc lamp with the total radiation focused onto the sample. Thus, during illumination, considerable temperature increments were developed on the sample, (as readily admitted by the authors). No attempt was made to determine wavelength dependence of the observed reactions. It is clear that thermal effects obviously played a very large part in all of the experiments. Other problems to be concerned with about the data are typified, for example, by the fact that easily discernible partial pressure changes of 10^{-14} Torr are presented. It is well known that this is not possible with an in-line quadrupole mass spectrometer, the type used in their experiments. With all of these limitations, it becomes virtually impossible to correlate the results in this paper concerning the UV induced oxidation of CO on ZnO to other reports on photodesorption.

Obviously, much complex chemistry is occurring during all of their experiments, and it is difficult to sort out which, if any, of their data relates to true photodesorption. Some typical data from this report can be seen in Fig. 14.

In 1975, the first of a series of papers appeared describing the work on ZnO performed in our laboratory⁴⁵. In this paper the results of careful mass analyzed photodesorption data from powdered ZnO samples is described. The main points in this paper are the following: true photodesorption is clearly established. Wavelength dependence measurements indicate clearly a threshold at the material band gap. In this paper, the photodesorption of primarily CO₂ and small amounts of oxygen is presented, see Fig. 15. (It has since been determined that the small atomic oxygen component is only a fragment of the CO₂ and that CO₂ is the only photodesorbing species.) A relatively high cross section is determined indicating values of approximately 10^{-17} cm^2 at the onset of illumination. The overall conclusions of this work result in reaffirming the following aspects of earlier models. One is the need for oxygen to prepare or rejuvenate the surface. The second is the need for band gap radiation to produce photodesorption. This radiation creates electron-hole pairs, the holes apparently migrating to the surface to recombine with the chemisorbed component, resulting in the observed photodesorption. The single, but very significant, break with previous ideas is the fact that it is CO₂ which photodesorbs and

not atomic or molecular oxygen and that it is CO_2 photodesorption which is responsible for the conductivity changes. If one now reviews the previous papers, discussed above, one finds that when photodesorbed species were mass analyzed, they invariably turned out to be CO_2 . Thus, our results, although quite surprising to the scientific community, are actually in good agreement with the few previous mass analyzed observations. What apparently occurred for many years was the idea of photodesorbed oxygen was so strong that observations of photodesorbed CO_2 were dismissed as extraneous.

Thus, the overall picture of the process as we consider it today, seems to be the following. Molecular oxygen, arriving at a semiconductor surface such as ZnO , CdS , TiO_2 , etc. adsorbs onto a carbon impurity atom, takes an electron from the conduction band to produce a chemisorbed " CO_2^- " complex and simultaneously causes a reduction of the surface conductivity. With radiation of band gap energy or above, electron hole-pairs are formed. Some of the holes, migrating to the surface, can recombine with the CO_2^- complex. This recombination leads to a physisorbed CO_2 molecule which is then thermally desorbed and simultaneously causes an increase in surface conductivity. The activation energy for this overall photodesorption process is measured to be about 0.25 eV for ZnO ⁴⁵. At this stage, the chemisorption of oxygen seems clear, the requirement for band gap radiation and the photodesorption of CO_2 molecules is well established. The details con-

cerning the nature of the carbon and the carbon complexes are not well understood.

3. In this section we will consider briefly a number of papers which, although they do not describe specific measurements of photodesorption, do, however, provide some useful background information which is helpful in attempting to determine the overall mechanism of photodesorption. Specifically, this group of papers involves measurements of surface conductivity and/or chemisorption.

The first paper in this group is that of Medved⁹ which appeared in 1961, and which was concerned with conductivity and chemisorption kinetics on sintered ZnO. This and subsequent papers provide useful information on the oxygen chemisorption kinetics and the role of charge carriers in the substrate during surface reactions. Specifically, this paper is concerned with the model of adion formation by the capture of photoconduction electrons. In 1965, two further papers by Peter Mark appeared^{13,14} describing work on CdS crystals. Again, only indirect measurements are involved and only assumptions concerning photodesorbed species are possible. In these experiments, insulating samples were used. This factor makes it difficult, if not impossible, to draw any quantitative information from these measurements. This is because, (among other problems), with illumination both types of carriers are present, and chemisorption due to electron capture by neutral oxygen molecules and desorption due to hole capture by charged

molecules proceed simultaneously⁴². The following year, 1966, a paper by Van Hove and Luyckx¹⁶ described photoconductivity measurements on ZnO crystals in oxygen atmospheres. The contribution here is related primarily to chemisorption kinetics, determined by observing the variation of the photo-current decay rate with increasing oxygen pressure.

In 1968, an interesting paper by Hoenig and Lane²⁰ appeared. This was again primarily a study of the chemisorption of oxygen on ZnO. Their results supported the charge-transfer model of chemisorption by measurement of the effect of external d-c fields on electron migration to the surface. Of interest is a short comment in the paper about observing photodesorption from thin films of ZnO with sub-band gap light. Unfortunately, very little information is provided about how the photodesorption is detected and since no further work in this area has come forth from these workers, we are not able to comment on the significance of these particular results.

In 1970, we find a lengthy paper by Weber²⁸ in which chemisorption and, supposedly, photodesorption kinetics are studied by measurement of conductivity changes on CdS crystals. Extensive data and elaborate calculations are presented. Unfortunately, insulating samples were again used so that both chemisorption and photodesorption are simultaneously involved in many of the experiments. Thus, the analysis is quite complicated and provides little helpful information in understanding the details of the

overall process, although qualitatively there is a quite reasonable general discussion of the adsorption and desorption process. The assumption that it is oxygen which is desorbing is again carried through.

In 1972 we find a short paper by Chong, Connoy and Mark³³ describing a study of chemisorption on powdered ZnO. They worked with both CO and oxygen adsorption, proposing that CO is an acceptor-like adsorbate. It seems most probable that the observed conductivity changes which they attribute to CO adsorption is due to O₂ impurities in the gas used. In 1973 a theoretical and experimental paper appeared by Arijs and Cardon^{35,36} which again considered chemisorption kinetics of oxygen on ZnO single crystals. Both papers deal only with oxygen chemisorption. Photodesorption enters only by way of preparing the accumulation (high conductance, space-charge) layer prior to the chemisorption measurements. Therefore, no data relevant to the photodesorption process itself is available in these particular papers.

The primary value of this group of papers is the development of further evidence and verification of the oxygen chemisorption process and its clear cut correlation with surface conductivity changes. Since this process is the precursor to the photodesorption event, the results in these papers are useful in arriving at conclusions concerning the overall process. Due to their indirect nature, however, they cannot characterize the chemisorption mechanism or adsorption sites in any specific way.

4. The following four papers also provide some information on the overall oxygen-semiconductor system, utilizing a number of different experimental techniques. The first, by Many, Shappir and Shaked²³, appeared in 1969 and involved the study of oxygen adsorption on CdS surfaces by field-effect measurements. Here we find additional specific correlation between the adsorption process and electronic processes in the semiconductor. A second paper by Shappir and Many²⁴, appeared the same year and considered oxygen adsorption and desorption processes studied by surface photo-voltage measurements, again on CdS samples. The use of semiconducting (and not insulating) samples had considerable advantage in that both chemisorption and photodesorption could be more readily analyzed. This paper contains a good analysis of the data. A rate equation is developed which describes quite well the desorption process assuming recombination of photo-generated holes with electrons trapped in chemisorbed molecules. In discussing the mechanism it is assumed that photodesorption involves the reaction:

Other than the fact that the chemical identity of the photodesorbed species is assumed, the data is in good agreement with the presently accepted overall process.

That same year, there appeared a paper by Kwan²⁵ in which photo-adsorption and photodesorption of oxygen on inorganic semi-

conductors was studied using ESR. Since no mass analysis of the desorbing species was undertaken the desorption of oxygen is again an assumption. The overall results obtained with ESR are consistent with the generally accepted picture that electrons and holes participate in the adsorption and desorption phenomena. The very strong persistent assumption in the literature that oxygen is the photodesorbing species led to the conclusion of this paper that the ESR data can be assigned to an O_2^- component on the surface. Unfortunately, this assignment is not unambiguous, but still it is something to be eventually explained.

In 1971, we have a paper by Schubert and Boer²⁹ who studied the oxygen-CdS system using thermally stimulated desorption. They claim that, working with CdS single crystal platelets, they observe no photodesorption but do see thermal desorption of O and H_2O . They also find considerable correlation of these results with the electrical properties of the samples. The data on the thermal processes are somewhat interesting but have little bearing on the photodesorption process. It is not clear why they were unable to detect any photodesorption, unless they neglected to look for any other species in the mass spectrometer, again following the assumption that if anything would desorb, it would be oxygen.

This group of papers is quite useful and interesting, primarily because they show that other experimental techniques tend to yield results which are in good general agreement with

the accepted theories developed from the previously described techniques of sections 1-3.

5. In this section we find a number of papers that provide peripheral information which is of some value in the overall study of photodesorption. The first is a paper by Heiland¹⁰ which deals mostly with the fast component of photoconductivity in ZnO (that is, the production and recombination of electron-hole pairs). Perhaps the most useful part of this paper, for our purposes, is that it contains a very good resumé of the state-of-the-art in photoconductivity up to 1961. Two papers by Nobbs^{18,19} deal with attempts at practical applications of ZnO in detecting atmospheric gaseous components. There is no relevant information to quantitative chemisorption or any photodesorption aspects, but the papers do show some of the problems involved in trying to utilize electrical conductivity changes in ZnO in a rather complex practical application.

Another paper by Heiland and Kunstmann²¹ provides a good general reference dealing with the basic properties of ZnO. A paper by Morrison²² in 1969 considers further measurements of electronic energy states in ZnO associated with chemisorbed species. Morrison produced large depletion layers by depositing ions from a corona discharge onto the ZnO surface. The value of the paper to us is in the discussion of the behavior of a semiconductor such as ZnO as regards the development and behavior

of surface states related to chemisorbed molecules.

Two papers, by J. D. Levine et al.³¹ and by Mark, et al.³², appeared in 1972 and considered the influence of surface structure on the properties of ZnO in one paper³¹ and CdS in the other³². The most significant conclusion from these papers is that when these materials are clean and atomically ordered, (as judged by AES and LEED) they are inert to oxygen chemisorption. These results are in good agreement with our proposed model which requires impurity carbon to start the overall process by allowing oxygen chemisorption. In 1974, we find a paper by Kokado, Nakayama and Inoue³⁸ concerning photoconductivity measurements on ZnO. This paper has little to do directly with our work on photodesorption. All experiments are conductivity measurements taken at pressures of 2 Torr and using adsorbed dyes. Its value is that it provides still further evidence on the correlation of surface reactions and substrate electronic properties. From 1974, we find a relatively short paper by Thevenet, Juillet and Teichner³⁶ which considers the oxidation of CO on TiO₂ surfaces subjected to UV radiation. Experiments are performed at relatively high pressures, in some cases at hundreds of Torr. Two rates of the reaction are observed and explained by 1) the reaction of adsorbed CO with lattice oxygen and 2) the reaction with adsorbed and dissociated oxygen from the gas phase. ESR measurements are again claimed to show the chemisorbed species to be O₂⁻. Irradiation is done in the wavelength range of 210-390 nm. Strangely, although the

point is repeatedly made that the reactions occur only during UV illumination, there is no discussion whatsoever about the role of the UV radiation in the process. No correlations are made with the UV radiation wavelength or intensity, so it is difficult to evaluate this data in order to compare it with other reports.

To complete this group, we have a paper by Kohl, Henzler and Heiland⁴³ concerning primarily sublimation processes from ZnO crystals. This paper is of no direct relation to photodesorption but does provide considerable useful information on sublimation processes from ZnO as a function of temperature.

The papers in this group, although not directly concerned with photodesorption, are nonetheless, useful in helping to develop the details of the overall process which must include chemisorption and the electronic properties of the semiconductors in addition to the actual desorption event.

6. Finally, we have a group of review papers. None of these papers is a review of photodesorption itself, but included in them is information which is relevant to this study. The first of these, appearing in 1959, is by Terenin and Solonitzin⁷. The paper starts with a short review of work done in the Soviet Union in this area up to about 1959. Experiments are described concerning two groups of substrates, namely metals and semiconductors. The metals can be divided as powders (Ni) and sublimed films (Zn, Cd, Sb and Bi). The only semiconductor discussed was ZnO. Experi-

ments were carried out in a static system at pressures of 10^{-2} to 10^{-5} Torr. Total pressure changes due to the irradiation of the samples were measured with a Pirani gauge. Pressure changes of 10^{-4} Torr were observed. Identification of desorbed gases was accomplished by observing if the desorbed gas condensed at -180°C . Three light sources were used, all were rated over 200W. Filters made from glass, mica, organic film, gelatine, calcite and cellophane film were used to separate the spectral lines of the sources. The illumination times were of the order of minutes to tens of minutes, which produced very slow pressure rises probably due to thermal desorption. The main value of this paper is in the description of the early Soviet Union work.

The next review was written in 1962 by Stone¹¹. This is a lengthy chapter in the Advances in Catalysis book series. The major portion of the chapter deals with chemisorption and the general chemistry of catalysis on metallic oxides. Near the very end of the chapter there is a short section on photo-adsorption and photocatalysis. This paper is a rather good review of the literature to that date and has a good bibliography list. Much of the discussion at the end of the chapter is related to photo-adsorption. In the photodesorption discussion, he basically repeated the assumption that oxygen is the photodesorbed species. Attempts were made to explain experimental results utilizing the assumption of oxygen adsorption and desorption. This chapter is primarily a very good review of the chemistry of metallic oxides,

and as such provides good background information.

In 1965 we find a significant review paper by Peter Mark¹⁵. This paper is a review of chemisorption on semiconductors. A model for photodesorption is discussed briefly. The n-type, extrinsic semiconductor model goes as follows: Initially, the surface of the semiconductor is considered chemisorbate-free, thus the energy bands are flat at the surface (no band bending), signifying that there is no net charge on the adsorbate (such as oxygen). Some of the electrons near the surface are spontaneously trapped by physically adsorbed oxygen to form negative ions on the surface. These ions are electrostatically compensated by the positive space charge of the immobile ionized donors distributed in the adjacent bulk and a Schottky-type surface barrier is formed. Chemisorption proceeds until the thermal release rate of the electrons from the surface ions back to the conduction band just balances their arrival rate. The rate-limiting step during chemisorption is considered to be the diffusion of the electrons through the Schottky barrier field. When the surface is now illuminated with radiation of energy equal to or greater than the band gap, hole-electron pairs are formed. The photoholes drift to the surface in the barrier field where they neutralize the adsorbed ions and the photoelectrons in the conduction band compensate the positive space charge of the ionized donors. Thus, photodesorption tends to restore the initial flat band configuration. The criterion for photodesorption to occur is that

In 1974, there appeared a short review paper on the theoretical aspects of photo-emission, photodesorption and photo-chemistry by Grimley⁴¹. The short section on photodesorption is very general and assumes that the interaction to study is only the direct interaction of the photon with the adsorbed molecule. Since we are now aware that this interaction is of least concern, the very limited discussion of this theoretical approach is not particularly relevant.

To complete this group we have a lengthy, detailed discussion of the relation between physical and chemical processes on semiconductor surfaces by Many⁴². This is a good, relatively current review which includes considerable material pertinent to the photodesorption study. As a review, it is not concerned so much with new material, but does provide a very good discussion of the state of understanding in this area up to 1974. Since this paper appeared before we had arrived at an appreciation of the importance of carbon in the overall process, its major value is in the very good discussions describing chemisorption, general photodesorption and the electronic processes involved in the substrate semiconductor. Most of the details are related to the CdS-oxygen and ZnO-oxygen systems.

In each of these review papers, the discussion of photodesorption is a relatively minor aspect of the overall paper. However, they all provide excellent reference lists and overall discussions which would be quite helpful to anyone interested in learning more about the details of semiconductor behavior in this area.

PHOTODESORPTION - Reference List - Semiconductors

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PHOTODESORPTION - Figure Captions - Semiconductors

- Fig. 12: Typical trace for photodesorption in baked ZnO powders from the work of Medved. Note the very slow response times indicating that the data is most probably related to thermal effects. (Adapted from Ref. 5)
- Fig. 13: Typical photodesorption curve from powdered zinc oxide sample. The authors assume the desorbing component to be oxygen. (Adapted from Ref. 8)
- Fig. 14: Pressure of CO₂ during alternating periods of illumination and darkness of the ZnO crystal. Crystal temperature 450C; 1000 W mercury arc. The data seems to indicate both photo and thermal effects. (Adapted from Ref. 44)
- Fig. 15: Composite mass spectra of gas phase in front of ZnO sample under dark conditions (dotted line) and under UV radiation (solid line). The primary change is seen at CO₂ (m/e 44). Increases are also seen at the CO₂ fragments at m/e 28 and m/e 16. (Adapted from Ref. 45)

FIG. 12

FIG. 13

FIG. 14

FIG. 15

IV. Conclusions

The work to date seems to clearly indicate that photodesorption from metallic surfaces is very inefficient or perhaps even non-existent. This fact seems to be true for wavelengths down to $2000 \text{ \AA}$ and for enough different metals such that it is probably universally true for all metallic surfaces. It seems that two areas require additional work. The first aspect should involve a more thorough testing of metallic surfaces in the wavelength range below $2000 \text{ \AA}$, and preferably to as low as $100 \text{ \AA}$. That wavelength range should determine rather completely the probability of photodesorption from metals if it exists at all. (The effect of very short wavelength radiation, i.e. less than $1 \text{ \AA}$, has been studied by Kaminsky et al. at Argonne National Laboratories.) The second aspect should be a theoretical analysis to attempt to determine why photodesorption from metals has such an unexpectedly low cross section.

In semiconductors, a relatively detailed mechanism has been proposed. It will be useful to complete the theoretical analysis to correlate specifically with the experimental data. From the point of view of the CTR program, the extension of this aspect of the research should be directed to studying photodesorption from metals which are slowly oxidized so as to produce a semiconductor-like surface film. It will be important to determine whether this oxidation process leads to a detectable

photodesorption signal from previously non-photodesorbing metals.

The completion of the additional projects mentioned should enable one to make relatively complete quantitative statements about photodesorption and to provide the numbers of concern to the appropriate design engineers.

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