

Photo-e.m.f. measurements on oxides

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Various metal oxides were investigated using laser pulse photo-electromotive force measurements. This method is possible if the band gap of these oxides is smaller than the laser radiation energy. The sign of the photovoltage and its decay rate depend on the specific surface potential, which is influenced by adsorption layers. The adsorption of acids and bases on ZnO, TiO₂, α-Fe₂O₃ and γ-Fe₂O₃ microcrystals shows the dependence of the photovoltage on the type of space charge layer on the surface of the oxides. Oxides with a depletion layer exhibit a rising photovoltage with rising pH, whilst oxides with an accumulation layer at the surface exhibit the opposite behaviour.

1. Introduction

The measurement of photocurrents and photovoltages is used in the investigation of materials for solar energy production [1–3], photographic materials [4, 5] and other photoactive devices [6]. Surface properties can influence the activity of those materials in an important way [7], and therefore investigation of surface properties by photocurrent/voltage measurements was undertaken.

The purpose of this work was to clarify the influence of surface properties on photo-electromotive force (e.m.f.). It was supposed that the main reason for the occurrence of a photovoltage in our experimental setup was the existence of a space charge layer on the surface of the microcrystals. Three different types of space charge layers can exist on the surface of semiconductors [7].

Fig. 1 shows charge density, electric potential, energy levels and the surface charge of the accumulation and depletion layer of an n-type semiconductor. The third type of semiconductor surface is the inversion layer. This is a special kind of depletion layer, in which the charge density of the majority charge carriers on the surface is lower than the charge density of the minority charge carriers.

On irradiation of the semiconductor surface with light of energy greater than the band gap of the semiconductor, electron and hole generation takes place, especially near the surface. The electrons and holes generated can recombine or move to the surface or bulk of the semiconductor. Band bending is probably the cause of the opposite movement of the electrons and holes and therefore the origin of the photovoltage. In the dark, under thermal equilibration, the chemical potential of the electrons is equal to that of the hole, and corresponds to the Fermi level of the solid. Under irradiation the chemical potential of the electron becomes different from that of the hole. As a result, the Fermi level splits into two quasi-Fermi levels, one for the electron and one for the hole. This is

illustrated in Fig. 2. The band bending is then the cause of the charge separation [1, 7].

2. Experimental procedure

The apparatus was developed to investigate photo-physical properties of photographic emulsion layers. An earlier construction was described by Roewer and Rittmeyer [4]. The present arrangement is shown in Fig. 3. The probe is located in the measurement cell (Fig. 4). It is irradiated with a beam of a nitrogen impulse laser (IGT 50, power 50 kW, pulse energy 20 μJ, half pulse width 0.5 ns, λ = 337 nm). The photovoltage is measured and monitored by means of a digital oscillograph (Phillips PM 3375). A personal computer works as the control unit.

All chemicals were analytical grade and used without further purification. The crystal size of the oxides used was below 1 μm, and the thickness of the space charge layer was therefore large compared with the bulk of the microcrystals.

Suitable probe layers can be prepared in two ways. The common way is mix the probe powder in a polymer solution (polyethylene vinylacetate/cyclohexane) and cast thin films (thickness 200 μm). In some cases the powder may be pressed into stable tablets with or without KBr as a binding material commonly used for infrared probes in the press.

The transient photo-e.m.f. were kinetically treated for the rate laws:

$$\text{first-order} \quad dU/dt = k_1[U] \quad (1)$$

$$\text{second-order} \quad dU/dt = k_2[U]^2 \quad (2)$$

$$\text{and first- and second-order} \quad dU/dt = k_1[U] + k_2[U]^2 \quad (3)$$

The physical interpretation of a first-order rate law is

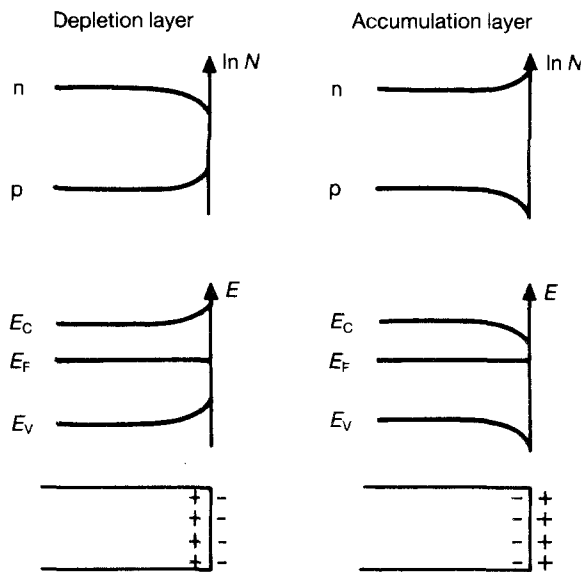


Figure 1 Charge density, energy level position and surface charge of the accumulation and depletion layer (N , number of charge carriers; p , n , number of holes and electrons; E_c , E_f , E_v , energy levels of the conduction, Fermi and valence band).

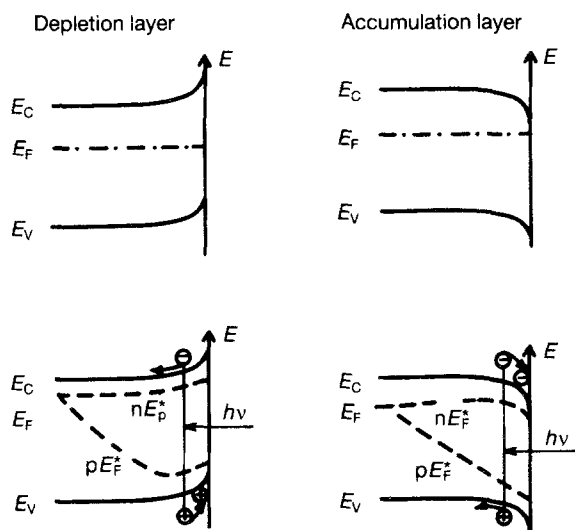


Figure 2 Illumination of an n-type semiconductor (nE_f^* , pE_f^* , quasi-Fermi levels of the electrons and holes).

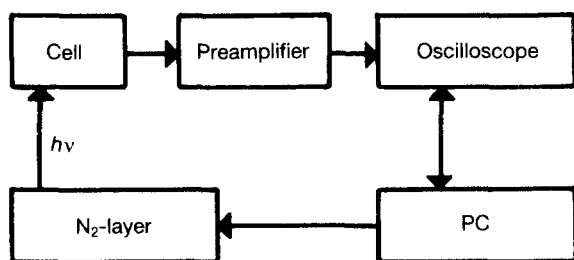


Figure 3 Experimental instrumentation for measurement of laser-induced photopotentials in layers.

that electrons are trapped. A second-order rate law represents a recombination of electrons and holes. The combination of these two rate laws corresponds to both processes.

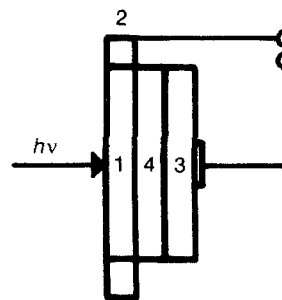


Figure 4 Construction of the measurement cell. 1. Quartz disc coated with tin oxide (front electrode); 2. contact ring of the front electrode; 3. back electrode; 4. probe.

In most cases, calculations with the second-order law exhibit the best correlations. The results of these calculations are U_0 (photo-e.m.f. at $t = 0$) and k_2 (rate constant). Some results of the oxides investigated are shown in Table I.

3. Results and discussion

3.1. Investigation of various oxides

A number of metal oxides are known as photoactive oxides. Many of them have been investigated especially for the light-induced cleavage of water. The most interesting and well-examined oxides are TiO_2 [11], ZnO [12] and Fe_2O_3 [3]. Some important electrochemical properties are given in Table I. This table also lists the photo-e.m.f. measured and the decay rate of oxides which were analysed (U_0 , k_2). This table contains only oxides which exhibit a photo-e.m.f. Also investigated were MgO , CaO , BaO , NiO , Al_2O_3 and Fe_3O_4 , CrO_2 , but these oxides show no photo-e.m.f. The reason for this behaviour is a metallic conduction mechanism, in the case of Fe_3O_4 and CrO_2 , or a band gap of more than 3.7 eV, where no electron and hole generation take place with a nitrogen laser as a light source.

The measurements show no correlation between the sign of the photo-e.m.f. and the conduction type of the semiconductors as supposed in earlier publications [14]. The decay of the photo-e.m.f. of some interesting oxides is given in Fig. 5.

Except for the well-known photoactive oxides ZnO and TiO_2 , a number of oxides exhibit easily measurable photovoltages. Very interesting and useful for the explanation of the origin of the photo-e.m.f. are the iron oxides haematite ($\alpha-Fe_2O_3$) and maghaemite ($\gamma-Fe_2O_3$). Both are n-type semiconductors with comparable band gaps, but the signs of the photovoltages are different. Several observations lead us to the assumption that surface properties, especially the surface charge, influence the photo-e.m.f. in a very strong manner. The isoelectric point is a scale for the charge on a surface. It seems that the sign of the photo-e.m.f. is closely connected with the occurrence of an acid or base surface on the oxide (Table I). If the IEP of an oxide is lower than 7, we observe a positive photovoltage. At higher IEP values negative values of the photo-e.m.f. (except ZnO) occur.

TABLE 1 Properties of some oxides investigated

Oxide	E_G^a (eV)	type	IEP ^b	E_{Fb}^c (V)	U_0 (mV)	k_2 (s ⁻¹ V ⁻¹)
CoO	2.6	p			-0.1	3.4×10^9
Cr ₂ O ₃	3.2	p	7.0 [9]		-0.6	1.8×10^5
CuO	0.6	p	9.5 [9]		-0.2	1.4×10^8
Bi ₂ O ₃	2.8	n			-0.5	5.9×10^5
α -FeOOH	2.1	n	6.7 [9]	-0.16 [10]	-1.2	4.0×10^7
α -Fe ₂ O ₃	2.1	n	6.7 [8]	-0.52 [10]	-1.7	4.0×10^4
γ -Fe ₂ O ₃	2.1	n	5.5 [8]	+0.02 [10]	1.2	4.0×10^7
Nb ₂ O ₃	3.9	n			-0.8	3.0×10^5
In ₂ O ₃	2.7	n			0.1	1.1×10^7
WO ₃	2.7	n			-1.6	1.8×10^5
ZnO	3.0	n	9 [9]		1.3	10^3 - 10^4
Sb ₂ O ₃		n			-2.7	3.3×10^1
TiO ₂ (rutile)	3.0	n	5.0 [9] 5.9 [9]		2.3	3.2×10^5
TiO ₂ (anatase)	3.2	n	5.0 [9]		4.4	6.5×10^4

^a E_G , band gap. ^b IEP, isoelectric point. ^c E_{Fb} , flat band potential (pH = 1).

Treatment of the oxides with acids or bases change the height and the decay of the photovoltage. This is another important indicator of the influence of the surface properties of the photo-voltage. The origin of the macroscopic photo-e.m.f. is a charge separation of the electrons and holes produced. Furthermore this charge separation rises with rising band bending. This observation was also made with photographic silver halide emulsions. The crystals with AgBr/AgBrI heterojunctions exhibit at the interface a very good charge separation and a high photovoltage [10]. Further experiments, especially surface modifications with acids and bases, support this hypothesis.

Other interesting properties are observed in the case of ZnO. The height of the photovoltage and decay rate depend on the length of the period of darkness between illumination impulses. Short intervals between laser pulses, 3 s for instance, display a strong decay of the U_0 value and an increase in the decay rate. Longer intervals (1 min) exhibit a moderate decay of the U_0 value. This behaviour is explained by the existence of deep traps [12]. These traps have a strong affinity with electrons and the pull-out is very slow. We suppose that the electrons trapped are located at or near the surface and the band bending of the depletion layer surface of ZnO could not be as high as it would

be without them. The photo-e.m.f., therefore, must decrease in the case of short light pulse intervals.

Very little is known about differences in the surface properties of the TiO₂ modifications rutile and anatase. We suppose that there are differences, because the photovoltage decays of these substances are quite different (Fig. 6). Anatase shows a higher photovoltage than rutile, but the decay rate is lower. Another cause of this different behaviour could be the different electrical resistances of anatase (0.5 - $2.8 \Omega\text{cm}$) and rutile (10^4 - $10^{12} \Omega\text{cm}$) and the different adsorption coefficients. Further experiments must be performed to clarify this problem.

3.2 Surface modification with acids and bases

The flat band potential of most oxides depends linearly on the pH of the solution [13, 14]

$$E_{Fb} = E_{Fb}(\text{pH} = 0) - 0.059V \text{pH} \quad (4)$$

This relationship is observed at semiconductor electrodes in contact with an adjusted solution. We have chosen a different approach, because the experimental apparatus is constructed for the investigation of solid layers. The investigation of the pH dependence of various oxides was performed according to the following procedure. A fixed amount of oxide was stirred into an acid or base solution. The pH of this suspension was controlled and adjusted for 1 h. The suspension was then filtered, but the filter cake was not

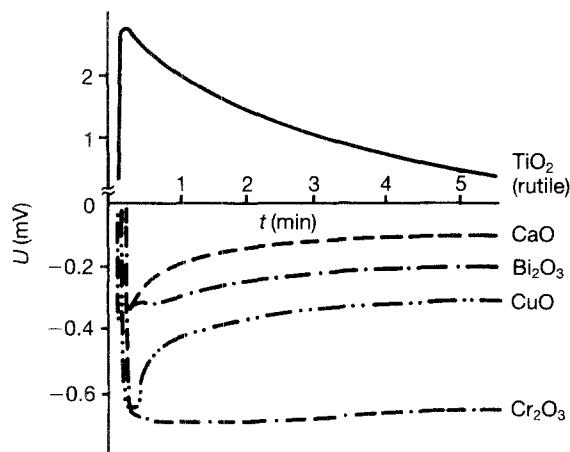


Figure 5 Photo-e.m.f. decay of various oxides.

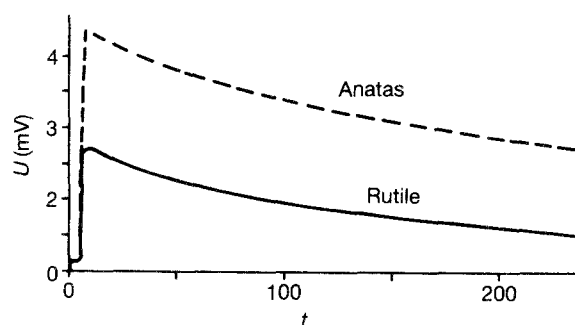


Figure 6 Photo-e.m.f. decay of rutile and anatase.

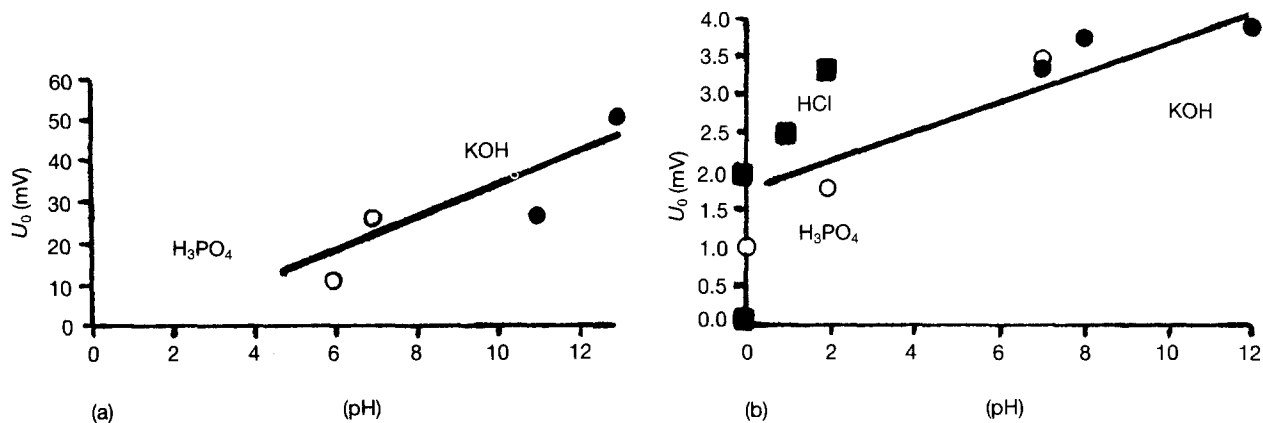


Figure 7 Influence of the adsorption of acids and bases on the photovoltage of (a) ZnO and (b) TiO₂.

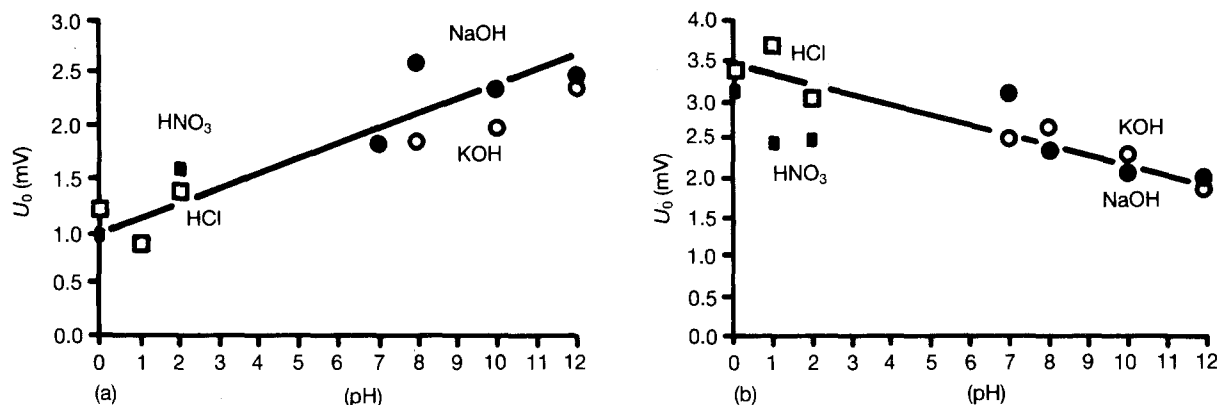


Figure 8 Influence of the adsorption of acids ((■) HNO₃, (□) HCl) and bases ((●) NaOH, (○) KOH) on U₀ of (a) γ -Fe₂O₃ and (b) α -Fe₂O₃.

washed. The net uptake of the potential determining ions H⁺ and OH⁻ rises almost linearly in many cases with the pH [15]. The surface charge and the band bending should thus exhibit the same effects.

When oxides with a depletion layer (γ -Fe₂O₃, TiO₂, ZnO) were used an increase of U₀ was observed with increasing pH. But the haematite (accumulation layer) displayed a decrease of U₀ with increasing pH. These results, shown in Figs 7 and 8, show very clearly the influence of adsorption layers on the photovoltages of the oxides observed. This behaviour can be explained as a displacement of the band edge using Equation 4.

In the case of an accumulation layer, the band bending falls with rising pH (dotted line in Fig. 9). The decreasing band bending should be the cause of a decreasing photovoltage, U₀. Haematite (α -Fe₂O₃) is an example of an accumulation layer semiconductor, and it exhibits this behaviour (Fig. 8).

A rising pH should increase the band bending of a surface with a depletion layer. ZnO, TiO₂ and γ -Fe₂O₃, for example, exhibit this effect (Figs 7 and 8). The degree of photovoltage growth with increasing pH also depends in some cases on the kind of acid or base. Possible explanations of this behaviour include the specific adsorption of some ions on the oxide surface or partial dissolution.

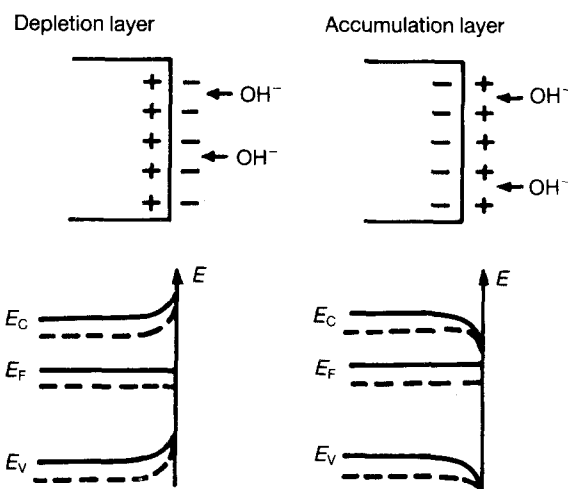


Figure 9 Influence of the surfaces treatment with bases on band bending.

4. Conclusions

The experiments demonstrate the possibility of investigating surface properties, such as band bending and surface charge, with photo-e.m.f. measurements. It is possible to investigate a large number of metal oxides. The main reason for the photovoltage observed is band bending on the surface of the microcrystals. This

band bending leads to a charge separation that can be measured as voltage. The direction of the band bending determines the sign of the photo-e.m.f. The photovoltage is influenced by surface treatment with acids or bases, which can be explained as the change of the band bending through surface charges.

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