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On the surface photoconductivity of sintered titanium dioxide pellet

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Surface photoconductance of sintered titanium dioxide (TiO_2) pellet has been studied at room temperature (306 K) and above (upto 475 K). Within the temperature range studied, the conduction in dark has been found purely extrinsic with the activation energies of 0.07 and 0.24 eV. Moderately slow growth of photocurrent at all temperatures indicated the presence of traps. Photosensitivity of the sample was found to increase continuously with the rise of sample temperature. Analysis of the photoconductive decay of the sample has revealed the existence of carriers with two different relaxation times (τ_1 and τ_2) which varied with the sample temperature in a peculiar fashion. © *1999 Kluwer Academic Publishers*

1. Introduction

Titanium dioxide (TiO_2) is well known for its photocatalytic and photoelectrochemical properties [1]. Photovoltaic effect has been observed for TiO_2-Zinc phthalocyanine composite cell [2] and also for copper phthalocyanine-titanium oxide heteromultilayer [3]. The photoconductive behaviours of thin TiO_2 films produced by different methods have been studied. Zhang *et al.* [4] have reported the formation of both rutile and anatase phase in thin TiO_2 films produced by spray pyrolysis of $TiCl_4$ at different temperatures leading to the variation of direct band gap in the range 3.5–3.7 eV. The surface property of TiO_2 thin film obtained by spray pyrolysis of titanium isopropoxide has been found [5] to change with the existing gases like oxygen, air and water vapour. Boschloo *et al.* [6] have studied thin anatase films prepared by metallorganic chemical vapour deposition. They found that initially insulating film could be made conducting by doping and from optical and photocurrent measurements estimated an indirect band gap of 3.26 eV. Report is also available [7] on the observation of superliner photoconductivity and a negative photoeffect in an inhomogeneous material consisting of a matrix of SnO_2 with nanometer-sized TiO_2 particles dispersed in it. Most of the works on photoconductivity of titanium oxide have been made either on single crystals or on thin films and no data is available on sintered layer of this oxide. TiO_2 being a material of technological importance, it was felt that studies on the optoelectronic properties of this oxide in the form of sintered layer may give some useful information and as oxides are more stable than the known semiconductors upto a fairly high temperatures, they are expected to serve as photo detectors at elevated temperatures [8]. In this paper we report our studies on the surface photoconductivity of sintered TiO_2 pellet in the temperature range 306 to 475 K and its photoconductive decay behaviour.

2. Experimental

AnalaR (Loba Chemie, India) grade TiO_2 (99.5% purity) powder was finely ground in an agate morter and pressed at room temperature (305 K) under a pressure of 6000 KPa using a hydraulic press. Pellets of diameter 1.5 cm and thickness 1.0 mm were used in the present study after sintering at 1050 K for 4 h in air. For photoconduction measurements, graphite paint was applied to one face of the pellet leaving a rectangular portion of width 3 mm along the diameter. The painted portions served as electrodes. The sample was then mounted on a heater and placed in a vacuum chamber (10^{-2} mm Hg) having a quartz window for the passage of light. Unfiltered radiation (intensity $L = 2200$ Lux) from a mercury vapour lamp was used for photoexcitation.

Constant voltage was applied to the sample using a transistorised DC power supply (Systronics, India, Model 613) and current was recorded using an Electrometer Amplifier (ECIL, Model EA815) in conjunction with DigiGraphic XY-recorder (Digital Electronics Ltd., India, Model 2000).

Before starting the photoconduction measurements, dark currents of the sample for different applied voltages were noted. The current was found proportional to the applied voltage, ensuring that good ohmic contacts were achieved with graphite paint. Temperature of the sample was maintained constant within ±1 K.

3. Results and discussions

Dark and photoconductance of the surface of sintered TiO_2 pellet were measured at different temperatures ranging from 306 to 475 K. The variation of dark conductance (G_D) and photoconductance (G_L) with temperature are shown in Fig. 1. G_D increased from its room temperature value of 5.94×10^{-12} mho to 1.69×10^{-10} mho at 475 K and the corresponding values of G_L were 4.75×10^{-11} and 4.16×10^{-10} mho

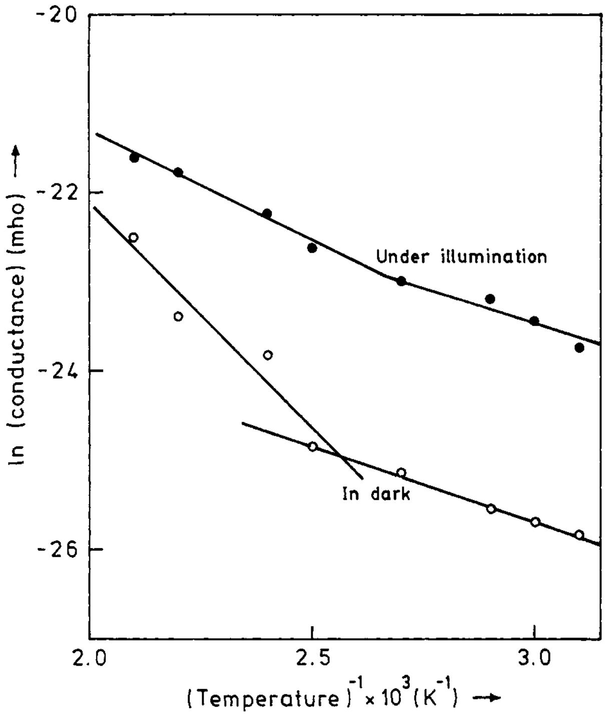

Figure 1 Variation of dark conductance (G_D) and photoconductance (G_L) with temperature (T) of the surface of sintered TiO_2 pellet.

respectively. Within the temperature range of study the conduction was purely extrinsic. The activation energies calculated from the slopes of the $\ln(G_D)$ versus $10^3/T$ curve were 0.07 and 0.24 eV respectively for the low and high temperature ranges. The ratio of the photoconductance to the dark conductance (G_L/G_D) has been found to increase upto 345 K and then decreased at higher temperatures. The maximum value of this ratio was found to be 10.5. The variation of photosensitivity ($\Delta G/L$) of the sample with temperature is shown in Fig. 2. It is interesting to note that the photosensitivity has increased continuously with rise temperature. The growth of photocurrent of the sintered TiO_2 surface was recorded at different temperatures (not shown in figure) upto 454 K. At all temperatures, the growth of photocurrent was moderately slow and took an additional minute to reach the saturation.

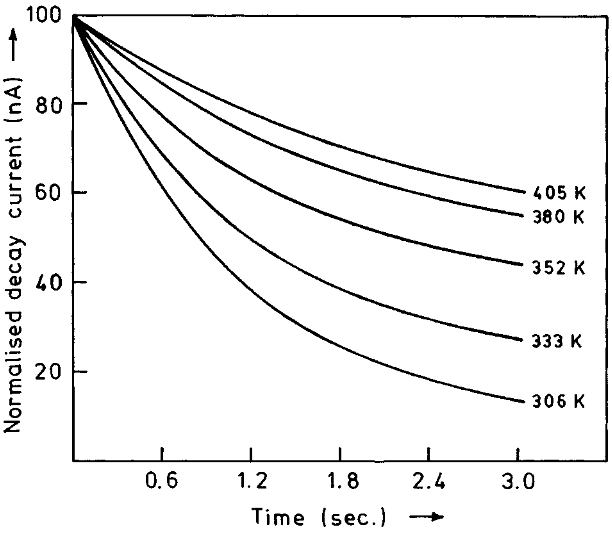

Figure 3 Normalised photoconductive decay characteristics of the sintered TiO_2 surface at different temperatures.

Decay of photocurrent of the sample was measured at eight different temperatures ranging from 305 to 475 K and some of them are shown in Fig. 3. The nature of decay has been investigated by plotting the logarithm of decay current $\ln(I)$ as a function of time (t). At all the temperatures, the decay curves were nonlinear. However, the $\ln(I)$ versus $\ln(t)$ plots were almost linear, which suggested hyperbolic decay of the type $I = I_0 t^{-b}$, where I_0 is the current at time $t = 0$ and 'b' is called the decay constant. Following Randall and Wilkins [10], such a decay can be treated as the superposition of exponentials corresponding to carriers having different relaxation times and may be written as

$$I = I_{01}\exp(-t/\tau_1) + I_{02}\exp(-t/\tau_2) + \cdots + I_{0n}\exp(-t/\tau_n)$$

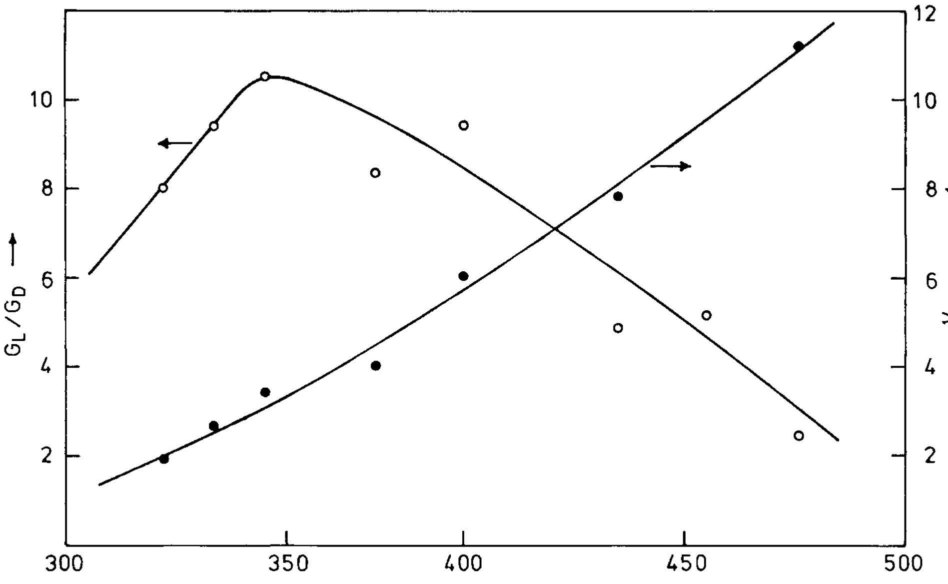

Figure 2 Temperature dependence of the photosensitivity ($\Delta G/L$) and the ratio G_L/G_D of the surface of sintered TiO_2 pellet.

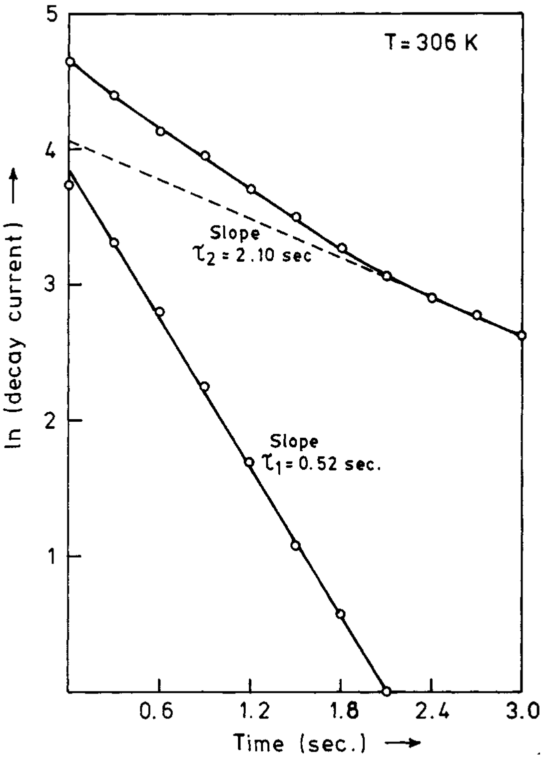

Figure 4 Splitting of the decay curve of the sample at 305 K by the "peeling off" procedure [12].

where I_{0n} is the decay current at zero time due to carriers having relaxation time τ_n. It is possible to split up such a decay curve [ln(I) versus time (t)] into a set of exponentials by the peeling off procedure as has been done by Bube [10] and Pawar *et al.* [11] in the case of afterglow decay in thermoluminescence. At all the temperatures, the ln(I) versus t curves were found linear for higher values of time. Assuming the decay for higher values of time to be composed of a single exponential, and starting with the higher time exponential and by successive subtraction of exponentials, it was possible to split the observed decay curve into a set of exponentials [12].

Splitting up of the typical hyperbolic decay curve of the sample at 306 K into two exponentials is shown in Fig. 4. From the slopes of the two resolved components the relaxation times τ_1 and τ_2 of the carriers were obtained. Similar analysis has been made for the decay curves at different temperatures (not shown in figure). The variations of τ_1 and τ_2 with sample temperature are shown in Fig. 5.

Titanium dioxide is an insulator having large band gap (>3 eV) and in an insulator at ambient temperature, the photoexcited excess carrier density is much larger than the thermal equilibrium carrier density. It is well known [13] that sintered pellets always contain inhomogeneities both on the surface and in the bulk, and photoconductivity in such materials is mostly controlled by the traps provided by the impurities and inhomogeneities. The observed moderately slow growth of surface photoconductance of the sintered TiO_2 pellet indicates the presence of traps which take part in the retrapping of the photoexcited carriers during excitation and remain operative at all temperatures under study.

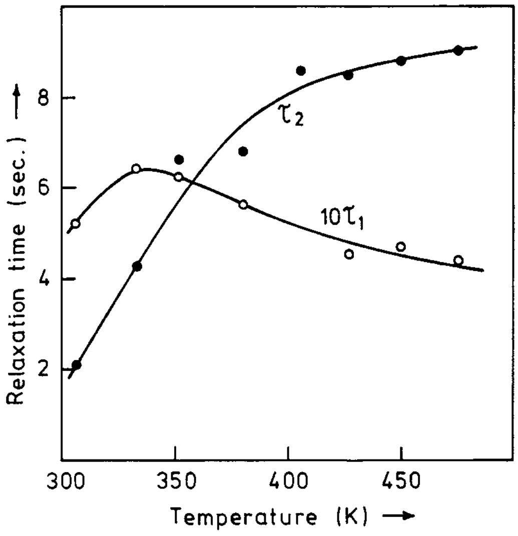

Figure 5 Variation of relaxation times (τ_1 and τ_2) with sample temperature.

Analysis of the photoconductive decay of the sample at various temperatures reveals the existence of two kinds of traps. As the sample showed reproducible values of dark and photo conductances even after repeated heating and cooling treatments (upto 475 K) under vacuum, the possibility of introduction of new traps due to oxygen desorption can be ruled out. The relaxation times τ_1 and τ_2 of the carriers are related to the two kinds of traps which were developed in the sample due to impurity incorporation and the inhomogeneities produced during pressing and sintering.

The initial part of the photoconductive decay is governed mostly by the carriers with relaxation time τ_1 while the later (time) part by the carriers with relaxation time τ_2. τ_1 has been found to increase with sample temperature upto about 335 K and then decreased at higher temperatures. This behaviour is not in accordance with the common concept that the relaxation time should decrease with increase of temperature. This peculiar variation of relaxation time τ_1 with temperature suggests that in the decay process not only the surface recombination but also the bulk recombination of the carriers determine the effective value of the relaxation time at any temperature. The effective relaxation time τ_{eff} in such case is given by [14]

$$\tau_{\text{eff}}^{-1} = \tau_{\text{s}}^{-1} + \tau_{\text{b}}^{-1}$$

where τ_{b} and τ_{s} are the life times of the carriers in the sample due to bulk and surface recombinations respectively. It is known [15] that for a photosensitive material $\tau_{\text{b}} > \tau_{\text{s}}$ and for an insensitive material $\tau_{\text{b}} < \tau_{\text{s}}$. In the present sample, for temperatures below 335 K when $G_{\text{L}}/G_{\text{D}}$ is more, τ_{eff} will be nearly τ_{s}. That is, below 335 K the surface recombination is predominant. For temperatures above 335 K, the ratio $G_{\text{L}}/G_{\text{D}}$ is low and τ_{eff} will be nearly τ_{b} and hence the bulk recombination is more pronounced. Therefore the variation of τ_1 over the entire temperature range can be divided into two (i) below 335 K and (ii) above 335 K. For temperatures below 335 K where the surface recombination is dominant we find τ_1 to increase with temperature. A two-center model [16] seems to be applicable in this temperature range. With the rise of temperature the Fermi level and the hole demarcation level come closer causing the density of recombination centers to decrease and hence relaxation time τ_1 to increase. For temperatures above 335 K when bulk recombination dominates, the relaxation time τ_1 decreases with rise of temperature. This can be understood from the barrier theory of photoconductivity where the variation of relaxation time (τ) with temperature (T) follows the relation [13]

$$\tau = \tau_0 \exp[E_{\mathrm{rec}}/kT].$$

But the relaxation time τ_2 of the carriers responsible for the later part of decay has been found to increase continuously upto 475 K without any tendency to decrease. That is, above 335 K, when the carriers of relaxation time τ_1 undergo bulk recombination, the carriers of relaxation time τ_2 continue with surface recombination. The increase of relaxation times (τ_1 and τ_2) of the carriers upto a temperature of 335 K manifests itself as the increase in photosensitivity ($\Delta G/L$) (Fig. 2). The increase of photosensitivity above 335 K can be understood if we consider that above 335 K the increase of drift mobility (μ_d) of the carriers (of relaxation time τ) with temperature is much more than the decrease of relaxation time and the photosensitivity which depends on the product $\mu_d\tau$ increase with temperature.

4. Conclusions

The surface photoconduction behaviour of the sintered TiO_2 pellet is controlled by the presence of traps arising out of inhomogeneities and impurities. Over the temperature range of study (306–475 K), the photoconductive decay behaviour is governed by the recombination of two kinds of trapped carriers and both surface recombination and bulk recombination of the carriers remain operative. Although the photocurrent is very low ($\approx 10^{-9}$ A), the sintered TiO_2 surface can be used as a photoconductor at elevated temperatures (upto 475 K) where other semiconductors fail.

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