PHYSICAL REVIEW B VOLUME 25, NUMBER 6 15 MARCH 1982

Photoelectric properties and the energy gap of SiO_2

R. Evrard and A. N. Trukhin*
Université de Liège, Institut de Physique B5, B-4000 Liège, Belgium

(Received 18 September 1981)

The difference in the photoelectric spectra of SiO_2 obtained by different authors is shown to be due to the secondary current injected by the metal electrode when this latter is in direct contact with the insulator. The photoelectric response obtained with blocking electrodes as well as the comparison between the afterglow properties and the decomposition of excitons in SiO_2 indicate a band gap of about 11.5 eV.

I. INTRODUCTION

The value of the band gap in SiO_2 is still a matter of controversy. A good review of this question can be found in Ref. 1. The experiments usually thought of as giving the most direct measure of the band gap are based on photoelectric properties of the material under study. However, different authors obtain completely different photoelectric spectra.[1–4]

This situation is not totally unexpected. Indeed, it is well known that the photoelectric properties of insulators are quite complicated, far more than those of semiconductors. The interpretation of these photoelectric properties and the determination of the band gap are thus subtle questions, the answers to which are not obvious. This is the reason why, in the case of the alkali halides, the history of obtaining a correct interpretation of the photoelectric measurements spanned about four decades, from the first measurement[5] to a satisfactory understanding in terms of exciton processes.[6]

The problem is to separate the internal photocurrent, in which one is interested, from the external photoemission. Another source of difficulty is the charge injection at the electrodes. For alkali halides, these problems were solved by covering the sample with a transparent film which is not photoconductive in the range of photon energies used for the experiment.[6]

One of us (Trukhin) used a more or less similar experimental setup,[4] whereas other authors[1,2] used metal electrodes directly in contact with the sample. However, the shape of the spectrum obtained in that way is quite different. This difference is illustrated in Fig. 1.

For the correct interpretation of the photoelectric properties as well as for the correct determination of the band gap, it is crucial to understand the role of the electrodes and, particularly, the reasons for the difference in the photoelectric measurements when the electrodes are in contact or not with the sample. The present paper is devoted to this question.

II. EXPERIMENT

The internal photoemission of SiO_2 samples, about 3000 Å thick, grown on Si substrates by thermal oxidation in a wet atmosphere, has been measured with two different experimental setups. In the first one, the SiO_2 sample lies directly on the copper electrode and silver paste is used to ensure a good electric contact between them [see Fig. 2(a′)]. In the second setup a blocking electrode is used. This electrode is again a copper disk, but it is now isolated from the SiO_2 sample by a sheet of mica 0.1 mm thick [see Fig. 2(b′)]. The measurements have been performed using a Keithley 610C electrometer and a McPherson 225 half-meter vac-

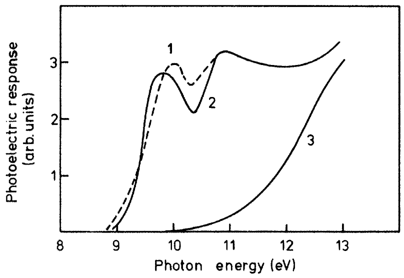

FIG. 1. Comparison of the photoconductivity spectra obtained by different authors. Curve 1 : DiStefano and Eastman (Ref. 2); curve 2 : Weinberg *et al.* (Ref. 1); curve 3 : Trukhin (Ref. 4).

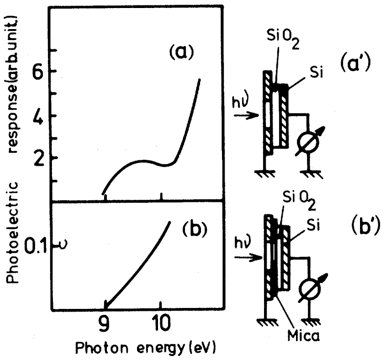

FIG. 2. Photoelectric response obtained with the electrode in direct contact with the sample (a), or with a blocking electrode (b). The corresponding experimental setups are shown in (a') and (b').

uum monochromator with a slit width of about 0.1 mm. The source of ultraviolet radiation is a hydrogen discharge lamp. In both setups, the sample is illuminated directly by the ultraviolet light through holes drilled in the electrode and screens. The back connection has been carefully shielded to avoid collecting unwanted electrons. To test the quality of this shielding, the contact at the back of the silicon substrate has been temporarily disconnected. As expected, no current is then recorded by the electrometer.

In the case of a blocking electrode, care has been taken that the radiation does not fall onto the copper or mica disks. When a direct contact is used, it is necessary to illuminate very near the edge of the electrode to obtain a response characteristic of injection phenomena. The current at zero voltage (except for voltage drop in the internal resistance of the electrometer) is recorded after the beginning of illumination of the sample by monochromatic ultraviolet radiation. The temporal behavior of the current is quite different when blocking or direct contacts are used. With the blocking electrode, the current reaches a maximum almost immediately and then falls back to zero in a more or less exponential way. The interpretation that comes naturally to mind is that, after a transient formation of space charge, the net motion of the charge carriers is prevented by the electric field due to this space charge. Subsequent pulses of radiation with the same frequency produce no current at all if they take place after not too long a delay. If the time between the pulses is long enough, of the order of one or several hours at room temperature, then the initial current and its temporal behavior is fully restored, showing that the space charge has completely vanished. The measurements at the different photon frequencies have been performed at large intervals of time, so that the space charge produced by the previous measurements has disappeared before new data are collected. The current at its maximum value is used as a measure of the photoelectric response of the insulator. A typical curve for this photoelectric response versus the energy of the incident photon is shown in Fig. 2(b). The response is weak and increases monotonically above the threshold located at about 9 eV. The detailed results, especially at higher energies, obtained with a blocking electrode have been reported previously.[4]

When a metallic electrode directly in contact with the insulator is used, the current increases slowly toward a stationary state which is reached in a few minutes. After the end of the radiation pulse, the current decays to zero with about the same time constant. A subsequent pulse leads to the same behavior for the current independently of the time delay, at least if one allows the current to go to zero between the pulses. This shows that the charges injected by the metal electrode (here, probably the silver contained in the silver paste) into the insulator cancel the space charge quickly. In the experiment with an injecting electrode, the stationary current is used to describe the photoelectric response of SiO_2. This photoelectric response is plotted as a function of the photon energy in Fig. 2(a). In the range 9 – 11 eV, not only is the current 20 to 40 times larger than with a blocking electrode, but also the shape of the curve is drastically different. This curve has now a maximum at about 9.6 eV and a minimum at about 10.2 eV. This shape has strong similarities with those obtained by the authors who have used metal electrodes directly in contact with the silicon dioxide (see Fig. 1). The only important difference is the relative strength of this first maximum of the spectrum, compared to the response beyond 10.5 eV. The difference could be due to the fact that, in the other works, the sample is illuminated by the ultraviolet radiation through the metal electrode, whereas, in the present work, the radiation falls onto the sample through the hole drilled in the electrode and, if it illuminates the metal, it is only on the edge of the circular hole.

III. DISCUSSION AND CONCLUSIONS

When a blocking electrode is used, the charge q flowing through the electrometer during each pulse of ultraviolet radiation is

$$q=q_i x/l$$

as shown in Ref. 7, p. 120, for instance. In this relation, q_i is the charge internally released, x the average distance traveled by the electrons before trapping, and l the distance between the electrodes. Since the lifetime of the holes is very short, they are assumed to be trapped at the place where they are produced. As there is no reason why the distance x should depend on the photon energy, the results of the experiment with a blocking contact should give a measure of the charge released by the direct photoelectric effect.

It is well known that, when a conducting electrode in direct contact with the sample is used, the measured current has two components: the primary and secondary currents (see, for instance, Ref. 7, p. 118). The primary current is due to the charge carriers released in the insulator. The secondary current is due to the injection of charge at the electrodes. This injection is made possible by the electric field associated with the space charge that builds up near the interface.

We interpret the difference between the spectra obtained with a blocking and a conducting electrode as due to this secondary current which predominates over the primary current when a conducting electrode is used. There are at least two arguments in favor of this interpretation. Firstly, the current is more than an order of magnitude larger than with a blocking electrode. Secondly, the current varies slowly towards the stationary value or towards zero when the ultraviolet radiation is turned on or off. The variation occurs typically in minutes. This is characteristic of the buildup or the decay of a space charge, as required for the injection to take place. Obviously, during the period of current decay, no primary current exists and, still, a large signal is observed for several minutes.

Therefore, we conclude that the curve of Fig. 2(a) in fact gives the photoelectric response of the secondary current injected at the electrode. To our knowledge, there is no straightforward way of obtaining the primary current from this result. Thus to deduce the value of the gap from the measure of the response when an injecting electrode is used looks most questionable.

The minimum in the current occurring at about 10.2 eV in Fig. 2(a) corresponds to a peak in the absorption spectrum (for the absorption properties see, for instance, Ref. 1). As suggested by Weinberg *et al.*,[1] it can be due to a strong reflectivity in this range of photon energies but the most probable mechanism is a higher recombination rate near the surface. The particles recombining can be free particles as well as particles bound in excitons.

We see no reason why the secondary current due to charge injection would not be important in all the experiments using conducting electrodes in direct contact with the sample. In Ref. 1, for instance, the way the current depends on the applied voltage is characteristic of charge injection and not of the primary current, as pointed out by the authors themselves. Definitive conclusions about the band gap could be drawn from the experiments using injecting electrodes only if one is able to separate the effects of the primary current from those of the secondary current due to charge injection. It has previously been clearly demonstrated[3,4,8,9] that the existence of excitons plays an important role in the optical absorption and energy transport in SiO_2. These excitons can decompose by many different mechanisms such as interaction with defects or effect of electric fields. This decomposition leads to an electron-hole pair and, therefore, is very difficult to distinguish from a band-to-band photoexcitation. Thus, to obtain information on the band gap, one should separate the exciton effects from those due to free electron-hole pairs. This seems possible in the following way.

On the one hand, Weinberg and Rubloff[9] have measured the charge accumulated at the Si-SiO_2 interface by decomposition of excitons. Thus their results can be considered as giving a direct measure of the number of excitons propagating in the silicon dioxide illuminated with ultraviolet radiation of different wavelengths.

On the other hand, one of us (Trukhin) has studied the afterglow of SiO_2 doped with copper, after irradiation by ultraviolet light.[8] He has obtained the intensity of the afterglow as a function of the photon energy of the exciting radiation. This af-

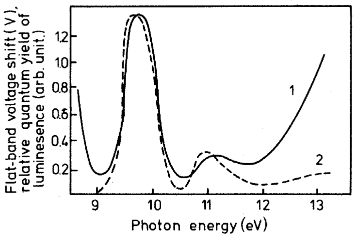

FIG. 3. Curve 1 : afterglow excitation spectrum of crystalline SiO_2 activated with Cu (Ref. 8). Curve 2 : spectrum of accumulation of positive charge at the SiO_2-Si interface (Ref. 9).

terglow has been interpreted as being due to copper centers excited either by excitons or by electron-hole pairs.

When both results are plotted together, with units such that the main peak has the same amplitude in both cases, one observes that they give very similar spectra in the region below 11 eV (see Fig. 3). Above this value, the afterglow spectrum increases rapidly, whereas the spectrum obtained by Weinberg and Rubloff[9] indicates a weak concentration of excitons. Therefore, it is quite natural to attribute the sharp increase in the afterglow spectrum as being due to the appearance of free electron-hole pairs on top of the excitons. That would locate the band gap somewhere between 11 and 11.5 eV. It must be noted that the spectrum of photoelectric response obtained by one of us (Trukhin) (see curve 3, Fig. 1), has a rather sharp increase in the same range of energy.

---

[*] Boursier R. C. I. in Belgium. Permanent address: Solid State Physics Institute, Stuchka Latvian State University, 226093 Riga, USSR.

[1] Z. A. Weinberg, G. W. Rubloff, and E. Bassous, Phys. Rev. B 19, 3107 (1979).

[2] T. H. DiStefano and D. E. Eastman, Solid State Commun. 9, 2259 (1971).

[3] Yu R. Zakis, A. N. Trukhin, and V. P. Khimov, Fiz. Tverd. Tela (Leningrad) 15, 216 (1973) [Sov. Phys.—Solid State 15, 149 (1973)].

[4] A. N. Trukhin, Phys. Status Solidi B 86, 67 (1978).

[5] A. Smakula, Z. Phys. 63, 762 (1930).

[6] G. R. Hugget and K. Teegarden, Phys. Rev. 141, 797 (1966).

[7] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948).

[8] A. N. Trukhin, Phys. Status Solidi B 98, 541 (1980).

[9] Z. A. Weinberg and G. W. Rubloff, Appl. Phys. Lett. 32, 184 (1978).