PHOTOCONDUCTIVITY OF V_2O_5-Si SANDWICH SYSTEM

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(Received January 5, 1976)

The photoconductivity of the V_2O_5-Si system was studied in the wavelength range 380 nm to 1000 nm. The results of measurements led to the conclusion that the major part of the photocurrent observed near to the fundamental absorption edge of V_2O_5 can be attributed to the vanadium pentoxide layer. The relation between photocurrent and light intensity was found to be linear with good approximation. On the basis of the experimental results, a simplified band diagram of the system is suggested. Illuminating the system by white light of high intensity, 0.3 V photovoltage was observed.

Introduction

Though vanadium pentoxide is a widely studied semiconductor, to our knowledge only one paper concerning its photoconductivity has been published to this date. I. HEVESI *et. al.* [1] found very weak photoconductivity of V_2O_5 single crystals illuminated by white light and by the light of a He-Ne laser. Observation of this weak photoconductivity is difficult due to the high thermal sensitivity of V_2O_5. The weakness of photoconductivity is supposed to be connected with the very high concentration of recombination centres in V_2O_5 crystals, which causes practically immediate recombination after generation of the carrier pairs produced by photons. We tried to reduce the effect of recombination by high electric fields on the V_2O_5 layer.

The present paper studies the photoconductivity of the V_2O_5-Si system and wishes to prove the photoconduction of the V_2O_5 layer in the region of the fundamental absorption edge of V_2O_5 on the basis of experimental results.

Preparation of the samples

n-type silicon single crystal plates of 10 mm×10 mm×0.2 mm with 1.3 Ωcm resistivity were used to prepare the samples, the polished single crystals being of (111) orientation perpendicularly to the 10 mm×10 mm plate. Ohmic contact was made on one of the silicon surfaces by phosphorus diffusion [2] and vacuum evaporation of gold; on the other surface a vanadium layer of 520 Å thickness was evapo-

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*Physical Department of the State University, Odessa rated in $5 \cdot 10^{-6}$ torr vacuum. The thickness of the layer was determined by a Thin Film Thickness and Deposition Rate Monitor type MSV-1841 made by the Hungarian Research Institute for Precision Engineering.

The silicon plates covered with vanadium layer were held in an oxygen stream of atmospheric pressure in an oven of 400 °C temperature for a week. For obtaining electric contact, a gold streak of ⊔ shape, about 1 mm wide and of 3 μ thickness was evaporated onto the yellow vanadium pentoxide layer formed during the oxidation process. Then a gold film of 500 Å thickness was evaporated to the interior of the ⊔-shaped streak (Fig. 1*a*, 1*b*).

a) *b)*

Fig. 1a. Front side of the samples: *a* free silicon surface; *b* free vanadium pentoxide surface; *c* gold electrode of 3 μ thickness; *d* semipermeable gold film of about 500 Å thickness .

Fig. 1b. Side-view of the structure: *a* semipermeable gold film; *b* gold electrode; *c* V_2O_5 layer; *d* Si plate; *e* Si layer with diffused in phosphorus; *f* gold back contact

In order to perform optical measurements, vanadium pentoxide layers were prepared also on thin quartz plates with the method described.

Experimental

The *I—V* characteristics of the samples were found to be assymmetrical [3]; on illumination under reverse bias remarkable photocurrents could be observed.

The experimental set-up used to measure the photocurrent can be seen in Fig. 2. Before performing the measurements, the dependence on wavelength of the energy of light coming from the monochromator was determined by a Zeiss thermocouple type VTh 8 MM, the knowledge of the energy permitting to relate the photocurrent measured to the same photon number.

In the measurements, the dark current of the samples was compensated and only the photocurrent was determined.

Fig. 3 shows the results obtained with the samples No. 1 and 2, by illuminating a 0.5 mm wide portion of the free V_2O_5 surface in the immediate vicinity of the gold streak at 4 V reverse bias. The abcissa gives the wavelengths in nm, the ordinate the photocurrents for the same photon number in arbitrary units.

Fig. 4 gives the results obtained by illuminating the samples through the thin gold film, under the same conditions as in Fig. 3. For comparison, the above measurements were made also with a silicon solar cell using the same electrode arrangement and the same conditions of measurements with the difference, that the reverse bias of the solar cell was 0.9 V. Fig. 5 shows the results obtained by illuminating a 0.5 mm wide portion of the free surface of the solar cell beside the electrode. While the relative photocurrent of the silicon *p-n* junction shows only one maximum at 900 nm, in Fig. 3 two maxima are seen in the curve of samples No. 1 and 2, at about 760 nm and 550 nm, and at about 800 nm and 560 nm, respectively. These maxima can be

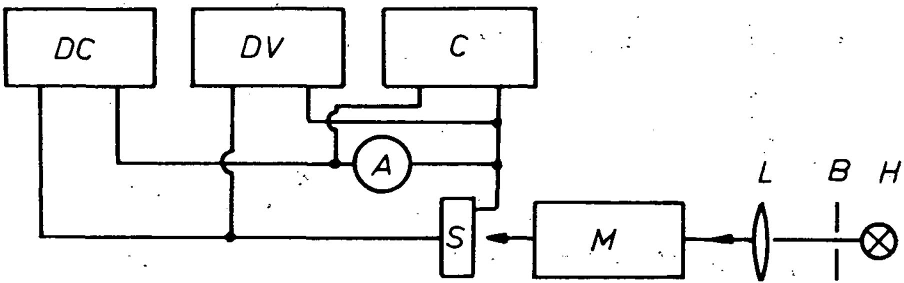

Fig. 2. Experimental set-up: *DC* current source; *DV* digital voltmeter; *C* compensator; *A* amperemeter; *S* sample; *L* lens; *B* diaphragm; *H* 150 W halogen lamp

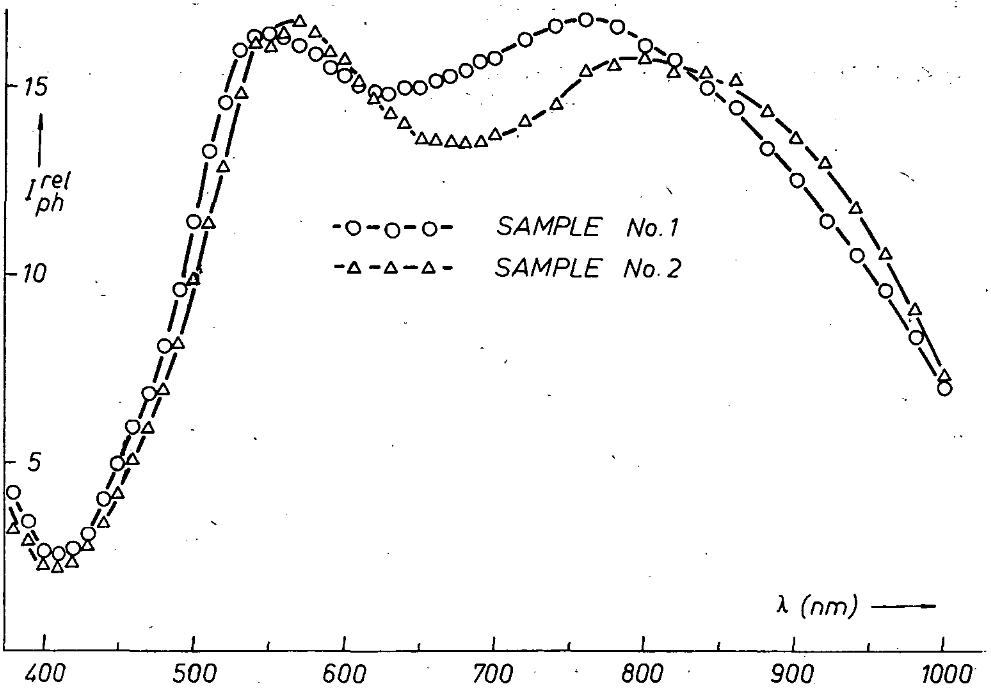

Fig. 3. Relative photocurrent *vs.* wavelength curves obtained at 4 V reverse bias by illuminating the free V_2O_5 surface in the immediate vicinity of the gold electrode

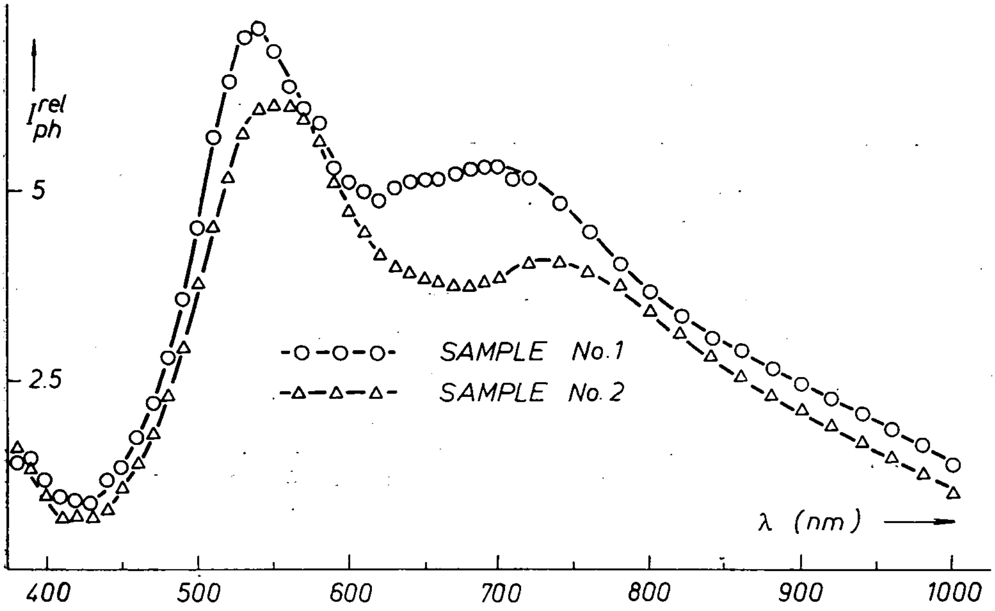

Fig. 4. Relative photocurrent *vs.* wavelength curves obtained at 4 V reverse bias by illuminating the samples through the gold film

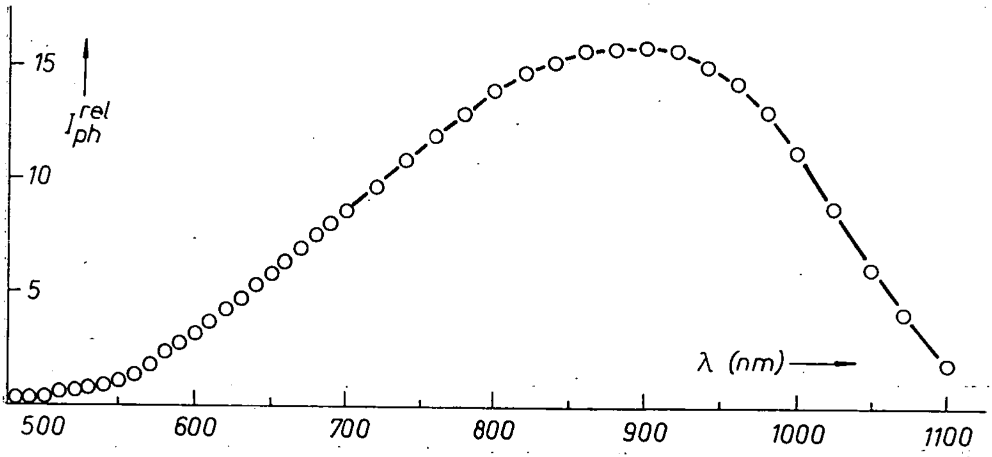

Fig. 5. Relative photocurrent *vs.* wavelength curve of a silicon solar cell

observed in Fig. 4 at about 700 nm and 540 nm, and at about 740 nm and 550 nm, respectively.

The dependence of the photocurrent on the reverse bias was measured on sample No. 1 with illumination by light of 1000 nm and 700 nm wavelengths. In Fig. 6 $\ln\frac{I_s+I_{ph}}{I_s}$ is plotted as a function of the reverse bias; I_{ph} means the photocurrent and I_s its saturation value. The results obtained by illuminating the free V_2O_5 surface are marked by open and full triangles, those obtained by illuminating through the gold film by open and full circles, respectively. Each curve of Fig. 6 shows a linear section, the extrapolation of which gives intersections with the abscissa corresponding to 0.56 V and 0.62 V, respectively.

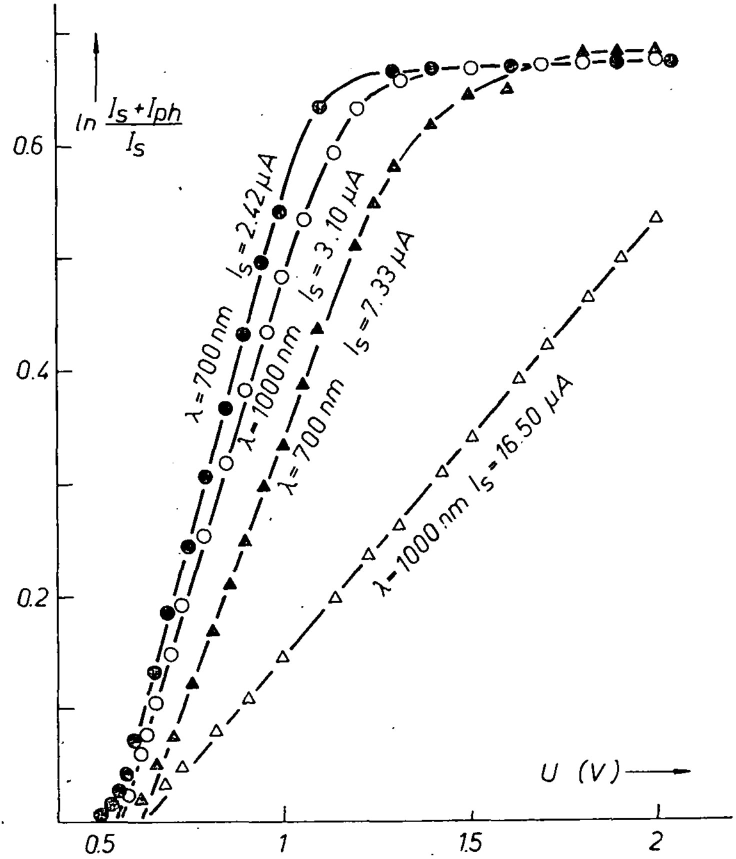

Fig. 6. Photocurrent *vs.* reverse bias curves. Open and full triangles: results obtained by illuminating the free V_2O_5 surface, open and full circles: those resulting from illumination through the gold film. I_{ph}: photocurrent, I_s saturation value of photocurrent

The relation between light intensity and photocurrent was measured by decreasing the light intensity by a calibrated grey wedge. The results of illuminating sample No. 1 at 4 V reverse bias with light of 550 nm wavelength are shown in Fig. 7. The results obtained by illuminating the free V_2O_5 surface are marked by circles, those of illumination through the gold film by triangles, respectively. The abcissas give the light intensities, the ordinates the photocurrents, both in arbitrary units.

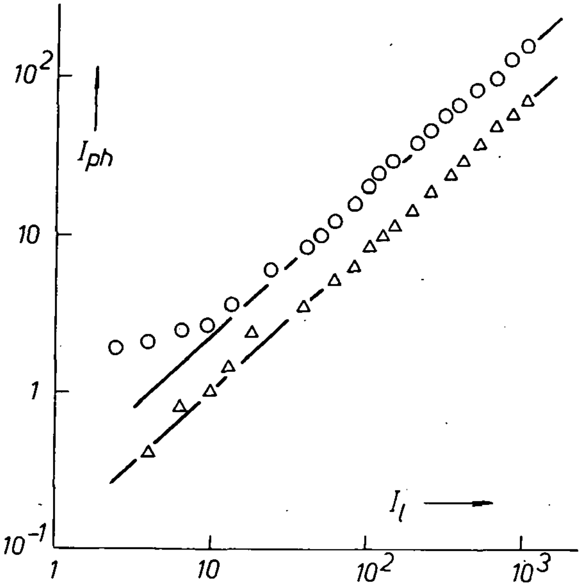

Fig. 7. Photocurrent *vs.* light intensity curves at 500 nm wavelength plotted in arbitrary units. Circles denote results of illumination of the V_2O_5 surface, triangles those of illumination through the gold film

The dependence on wavelength of the transmission of the gold film was determined by comparing the transmission of the mica mask used for the evaporation of the gold film with a mica plate of the same quality and thickness, using a spectrophotometer Optica Milano CF4DR. The transmission curve of the gold film shown in Fig. 8 was calculated from the transmission data of the mask covered with gold film and of the mica plate.

The transmission spectrum of the V_2O_5 layer of the samples was determined as described above using a V_2O_5 layer on a quartz plate, the layer being of the same thickness as that the V_2O_5 on the sample, and a quartz plate of the same thickness and quality than the quartz plate covered with V_2O_5. The results are shown in Fig. 9.

Illuminating the samples with white light of high intensity, a photovoltage of 0.3 V was obtained; the silicon side of the sample became negatively charged.

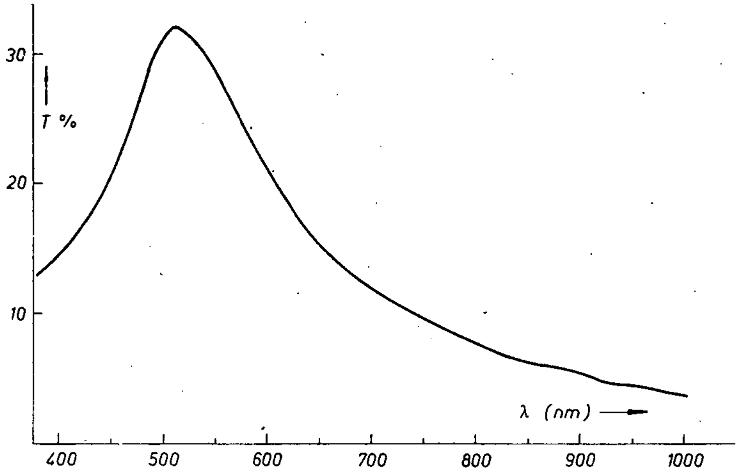

Fig. 8. Transmission curve of the gold film covering the V_2O_5 layer

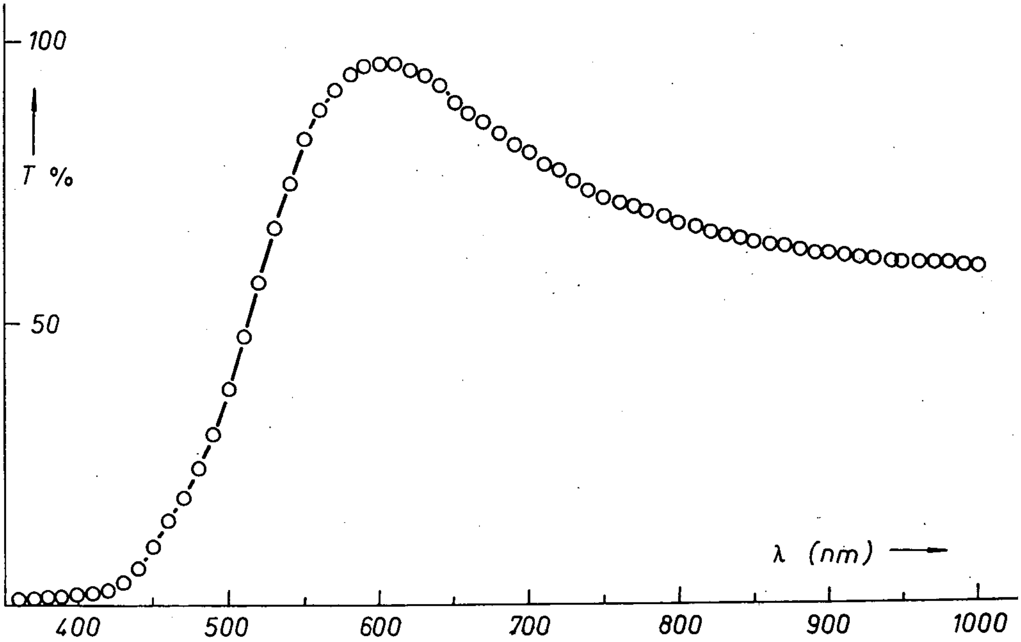

Fig. 9. Transmission curve of the V_2O_5 layer of the samples. Calculated thickness of the layer: ~0.16—0.18 μ

Conclusions

Taking into account the transmission curve of the gold film shown in Fig. 8, the deviation in the shape of the curves seen in Figs. 3 and 4, namely the shift of the maxima at longer wavelengths towards shorter ones and the increase in relative amplitude of the maxima at shorter wavelengths in Fig. 4, can be explained.

The thickness of the V_2O_5 layer on silicon plates was calculated to be 0.16 μ—0.18 μ, using the results of KENNEDY *et al.* [4] for the density of amorphous V_2O_5.

Comparing the transmission curve of the V_2O_5 layer shown in Fig. 9 with that obtained by SINCLAIR [5] for a sputtered V_2O_5 layer of 0.8 μ thickness, the agreement seems to be satisfactory, taking into account the difference in thickness. However, our curve appears shifted towards shorter wavelengths by about 70—80 nm compared with SINCLAIR's results.

From the photocurrent *vs.* reverse bias curves, presented in Fig. 6, the existence of a potential barrier between silicon and vanadium pentoxide can be deduced. Its height was found to be 0.56 eV from the intersections of the linear portions with the horizontal axis of the curves marked by open and full circles, respectively. The intersection of the two other curves is found at 0.62 V; however, the former value seems to be more probable, because the latter was determined by illuminating the free surface of the V_2O_5 layer, and in this case the voltage drop on the parts of free V_2O_5 surface not covered by the electrode may be noticeable, as shown also by the intersection of the curves at higher voltage.

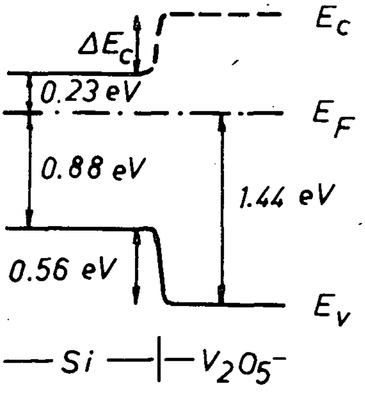

Fig. 10. Energy band diagram of the V_2O_5-Si system in first approximation

Taking into account the data concerning the position of the Fermi level and the band gap width of silicon of 1.3 Ωcm resistivity [6], the energy band diagram of the V_2O_5-Si system is given in first approximation[1] in Fig. 10. From the measured value of photovoltage it can be concluded that the value of ΔE_c is only slightly higher than 0.3 eV, so the band gap attributed to amorphous vanadium pentoxide is about 2 eV, lower than the 2.4 eV obtained for crystalline V_2O_5.

The photocurrent observed may be caused by carriers generated in the silicon and in the vanadium pentoxide layer alike. In order to separate both photoeffects, the relative photocurrents I_{ph}^{rel} pertaining to given wavelengths were divided by the transmission T of the V_2O_5 layer for the same wavelengths. The values obtained are shown in Fig. 11. Let us suppose that, at a given wavelength, N_0 photons arrive on the surface of the sample, and N photons on the V_2O_5-Si interface: then $N=N_0T$, $I_{ph}^{rel}=c\frac{I_{ph}}{N_0}$, where c is constant and I_{ph} is the photocurrent measured; $\frac{I_{ph}^{rel}}{T}=c\frac{I_{ph}}{N}$,

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[1] A more detailed band diagram to be described in [3].

If the reflexion on the interface is taken to be negligible, and the photocurrent. supposed for the moment to be caused only by photons absorbed in the silicon, then $\frac{I_{ph}^{rel}}{T}$ is proportional to the quantum yield. It seems reasonable to interpret the apparently marked increase of the quantum yield at wavelengths shorter than 500 nm as caused by the circumstance that in this wavelength range carriers are generated by photons also in the V_2O_5 layer.

With respect to the above, the relative photocurrent *vs.* wavelength curve shown in Fig. 3 can be interpreted as follows: at wavelengths longer than 500 nm

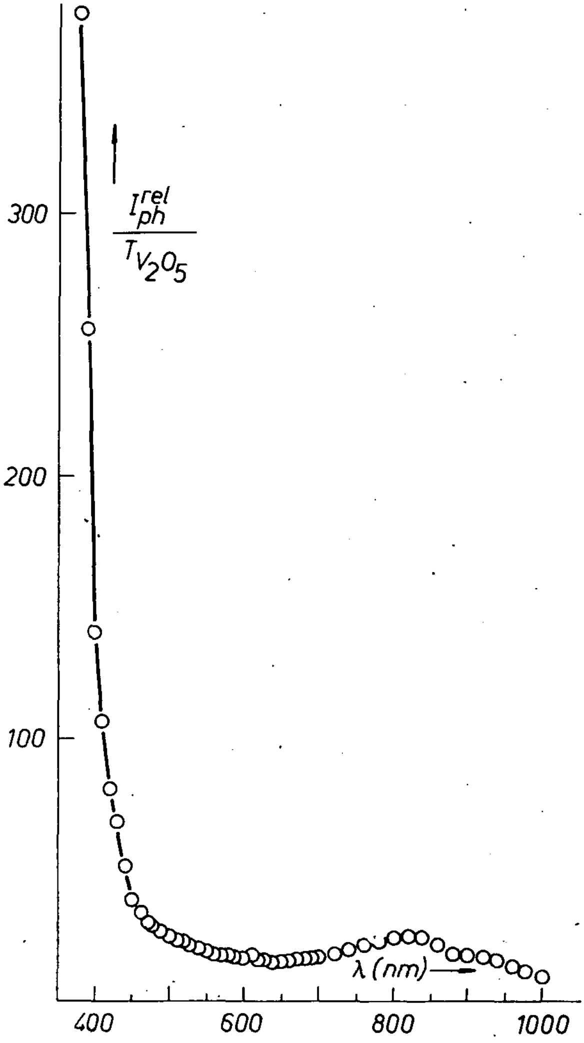

Fig. 11. The relative photocurrent divided by the transmission of the V_2O_5 layer

the photocurrent is mainly due to the silicon, the photoconductivity of vanadium pentoxide being important only at wavelengths shorter than 500 nm. The striking difference in the curves of Fig. 3 and Fig. 5 can be probably caused by the circumstance that the V_2O_5 layer acts as an antireflexive layer on the silicon, and thus the photocurrent of the silicon begins to decrease only at wavelengths shorter than 500 nm. The supposition of an antireflexive layer seems to be supported by the fact that in the wavelength region longer than 500 nm the value 1.8 was obtained for the refractive index of the V_2O_5 layer on the basis of literature data concerning the refractive index of crystalline V_2O_5 [8] and density values of amorphous V_2O_5 [4]; the refractive index of Si is surely higher than 3.42 in this wavelength range [6]. The decrease of the relative photocurrents towards shorter wavelength in the range 540 nm — 420 nm can be supposed to be due to the marked increase of the reflexion and absorption of the V_2O_5 layer (see Fig. 3 and 9); here the comparatively lower photocurrent from the V_2O_5 appears instead of the higher photocurrent of the silicon. At wavelengths shorter than 400 nm the increase in photocurrent may be attributed only to the V_2O_5 layer.

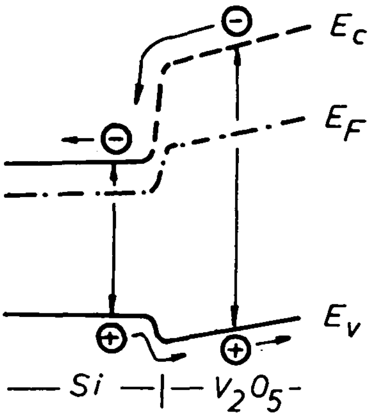

Fig. 12. Simplified mechanism of photoconductivity of the V_2O_5-Si system

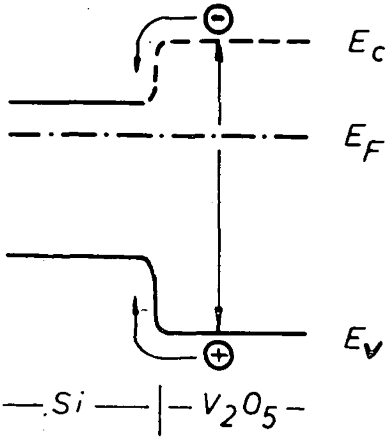

Fig. 13. The mechanism of photovoltage generation in first approximation

A simplified mechanism of the photoconductivity is shown in Fig. 12. From the electron-hole pairs generated by the light in the silicon, only the holes can pass the potential barrier lowered by the applied voltage, while from the V_2O_5 only the electrons are able to reach the silicon.

The mechanism of photovoltage generation is shown in first approximation in Fig. 13. Part of the holes and electrons generated in the V_2O_5 by the light diffuse into the silicon. The ratio of the electrons and holes reaching the silicon is approximately $\sqrt{\frac{D_n \tau_n}{D_p \tau_p}}$, where D_n and D_p are the diffusion coefficients, τ_n and τ_p the lifetimes in V_2O_5 of the electrons and holes, respectively. Vanadium pentoxide being a n-type semiconductor, the relations $D_n > D_p$; $\tau_n > \tau_p$ are valid. Thus the silicon must be charged negatively, as observed.

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ФОТОПРОВОДИМОСТЬ V_2O_5-Si СЭНДВИЧЕВЫХ СТРУКТУР

А. Шюли, С. Д. Курмашев, Л. Михайлович и И. Гевеши

Исследована фотопроводимость V_2O_5-Si системы в области длин волн от 380 до 1000 нм. На основании полученных результатов мы пришли к выводу, что, в области края собственного погащения V_2O_5, найденная фотопроводимость в основном обусловлена слоем V_2O_5. Зависимость между интенсивностью света и фототоком с хорошим приближением является линейной. На основании полученных экспериментальных данных составлена упрощенная диаграмма полос системы. При освещении белым светом большой интенсивности было найдено фотонапряжение в системе равное 0,3 вольту.