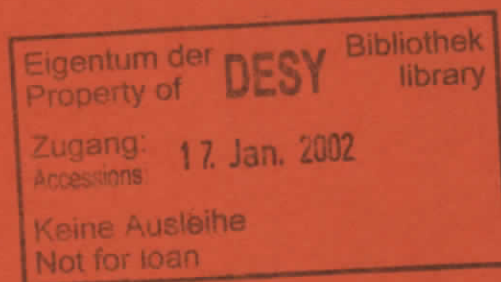


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IN THE VUV AND SOFT X-RAY RANGE

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SCHOTTKY TYPE PHOTODIODES AS DETECTORS IN THE VUV AND SOFT X-RAY RANGE

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ABSTRACT

The quantum efficiencies of semiconductor photodiodes have been measured at photon energies from 5 eV to 3500 eV. For silicon photodiodes strong radiation induced effects were found. GaAsP- and GaP- Schottky diodes show remarkable stability and high quantum efficiency. Applications of Schottky diodes for spectroscopic and radiometric measurements are discussed.

1. INTRODUCTION

Semiconductor photodiodes, originally designed for the visible spectral range, can also be used in the X-ray region¹. In the VUV- and soft X-ray region, however, the absorption lengths of all materials are very small, typical in the order of 20 - 200 nm. Therefore semiconductor detectors suffer from absorption losses in insensitive layers near the surface and thus have not been used so far. In a previous paper, however, we have demonstrated that 'UV-enhanced' semiconductor diodes make indeed very useful detectors for VUV and soft X-ray radiation²: the diodes are small, easy to operate, ultra high vacuum compatible, inexpensive, linear in response (up to 10 orders of magnitude) and, in contrast to photoemissive diodes, relatively insensitive to

surface contaminations. In the present paper we report on stability, quantum efficiency and sensitivity for various photodiodes.

Two types of semiconductor photodiodes are shown in fig. 1: a diffused diode and a Schottky diode. In the diffusion type diode a depletion layer is formed between the p- and n- doped layers, and in a Schottky diode at the semiconductor-metal interface. A photon, which is absorbed in the semiconductor, will produce a number of electron-hole pairs. The mean energy w required for electron-hole pair creation depends on the band gap of the semiconductor³. Experimental values for w are 3.61 eV for Si⁴, 4.2 eV for GaAs⁴ and 6.54 eV for GaP⁵. If these pairs are created in the depletion layer or if they diffuse into this space charge region they are separated by the internal electric field giving rise to an external photocurrent.

For diffused Si-diodes, the SiO₂-layer as well as most of the p-type material acts as a deadlayer with a typical thickness of 30 to 100 nm. For Schottky diodes, the deadlayer consists of the thin metal contact of about 10 nm. Since the absorption lengths in the investigated spectral region are very small, the response of the diodes is strongly reduced by the absorption in this layer.

The response of a photon detector is generally described by the quantum efficiency $\eta(E)$ or by the sensitivity $s(E)$. The quantum efficiency of a semiconductor photodiode is the number of electron-hole pairs created by an incident photon of energy E , while the sensitivity is the photocurrent per incident radiation power. Quantum efficiency and sensitivity are related by

$$s(E) = \frac{\eta(E) \cdot e}{E} \quad (1)$$

where e is the elementary charge. Because the mean electron-hole pair energy w is independent from the energy of the absorbed radiation ($E \gg w$), the quantum efficiency of a perfect semiconductor detector should increase linearly with the photon energy, while the sensitivity would be a constant, corresponding to the reciprocal of w . This behaviour is modified by absorption in the deadlayers, most important at low energies, and the penetration of photons through the space charge region at higher energies.

2. EXPERIMENTAL

The semiconductor diodes investigated here are commercially available photodiodes where the glass or silica window has been removed from the housing. They are operated in the photoamperic mode ⁶, usually without bias. The photocurrents, which are in the range from a few pA up to hundreds of nA were measured using a picoammeter (Keithley Electrometer 617).

As our measurements cover the spectral range from 5 eV to 3.5 keV, we used several monochromators at the synchrotron radiation centers BESSY and HASYLAB. The monochromators are listed in table 1, their performances are given elsewhere ⁷⁻¹⁰.

The semiconductor diodes were compared to the usual standard detectors (see table 1): The CsTe-diode with MgF₂-window and the Al₂O₃-diode were provided and calibrated by the NBS, the Au-diodes were produced by evaporating 0.1 μm Au on a stainless steel surface with a ring anode installed in front of the photocathode to remove the emitted photoelectrons. For the determination of the quantum efficiency, yield data of Henke et al. ¹¹ were used combined with measurements of Lenth ¹² and cross section data of Veigele ¹³. Additionally an ionisation chamber was used in the spectral range between 70 and 800 eV to check if these data hold up for our reference diode (see Appendix).

3. RESULTS AND DISCUSSION

3.1 STABILITY

A very important characteristic of all radiation detectors is the stability of their quantum efficiency. A great number of investigations has been carried out on the stability of semiconductor devices in ionizing radiation and in the UV range ^{14,15}, but little information on the stability of semiconductor photodiodes as detectors in the VUV and soft X-ray range is available. We therefore investigated the stability of about 10 different types of diodes in this spectral region ¹⁶.

The measurements on the stability of the efficiency were conducted with a monochromatic photon flux of about 10¹⁰ photons/s into an area of 1 mm² at a photon energy of 124 eV. Initially all diodes showed a quantum efficiency $\eta > 10$.

A typical behaviour of a silicon diode is shown in Fig. 2: The quantum efficiency decreases from the initial value of $\eta=27$ by 0.25%/s. The decrease of the efficiency shows a saturation behaviour, but even at $\eta=8$ a further decrease of the order of 0.01%/s is observed ^{16,17}. We have also investigated a Si-Schottky diode (type UDT PIN-10) with essentially the same result.

The stability of GaAsP- and GaP- Schottky diodes (Hamamatsu G1127-02 and G1963) was investigated in the same manner as the Si-diodes, and the results are also shown in Fig. 2. The quantum efficiency of both types of diodes is stable at least within 0.05% (which is the uncertainty of the measurement) during an exposure of more than 1 hour. Even in the intense zero order radiation of the monochromator no significant change occurred. The GaAsP-Schottky diodes have been investigated in detail by Wilson and Lyall ¹⁸ concerning their electrical properties and their optical behaviour in the spectral region below 6 eV. These diodes were found to be superior to Si-diodes in the UV-range. Due to this conclusion and our own stability measurements, the rest of this paper will deal only with GaAsP- and GaP-Schottky diodes.

3.2 QUANTUM EFFICIENCY AND SENSITIVITY

Our measured quantum efficiencies together with published data for the region below 6 eV (for diodes where the fused silica window has not been removed) ¹⁸ are shown in Fig. 3 for a GaAsP-diode; in this figure the efficiencies of the secondary standards used for the comparison are also inserted. In contrast to conventional detectors, the GaAsP-diodes can be used in the whole spectral region from 2 eV up to at least 3.5 keV. In the visible region the efficiency is comparable to that of photoemissive diodes, but it is higher by 3 - 4 orders of magnitude in the region above 1 keV.

In spectral regions where different monochromators were used, the measured efficiencies show differences up to 20%. The main problems are

the limited reproducibility of our secondary standards as well as the different spectral content of higher harmonics and stray light in the radiation of the different monochromators. For further discussion, we have derived average values for the measurements on different monochromators.

The spectral sensitivities of a GaAsP- and a GaP-Schottky diode are shown in Fig. 4 for the usual operation mode without bias as well as with a bias of 4.5 V. As mentioned in the introduction, the maximum sensitivity can be calculated from the mean electron-hole pair creation energy, which depends only on the semiconductor material. The values for s_{max} are 0.153 A/W for the GaP- and 0.182 A/W for the GaAsP-diode (using the composition $GaAs_{0.63}P_{0.37}$)¹⁸. The measured maximum sensitivities are close to these values.

The overall spectral dependence of the sensitivity is very similar for the two types of diodes. At low photon energies the sensitivity is strongly limited by the small transmittance of the gold layer in this spectral region². The gold transmittance also accounts for the valley between 150 eV and 500 eV, while the loss in the sensitivity at higher energies originates from the penetration of radiation through the depletion layer. In the high energy region an increase of the absorption of the semiconductor material therefore will result in an increase of sensitivity, as observed at the Ga L_3 absorption edge (1116 eV) and the P K absorption edge (2149 eV). The As L_3 absorption edge (1324 eV) appears only as a weak structure for the GaAsP-diodes. We attribute this to the nearly complete absorption directly above the Ga $L_{2,3}$ edge into which range the As L_3 absorption edge falls. Using the absorption data for Ga, P and As given by Henke et al.¹⁹, the thickness x_s of the depletion layer can be estimated as about 1 μm .

By applying a bias the sensitivity is increased in the low energy range by at most 10% due to the improved charge collection. At high photon energies the effect of a bias voltage is much more pronounced. The observed behaviour can be explained by the increase of the depletion layer caused by the bias. According to the theory of Schottky contacts²⁰, the thickness x_s is given by

$$x_s = \sqrt{\frac{2 \cdot \epsilon \cdot \epsilon_0 \cdot (V_0 + V)}{e \cdot N_d}} \quad (2)$$

with ϵ ϵ_0 being the permittivity of the semiconductor, V_0 the height of the

Schottky barrier (≈ 1 eV, depending on the materials), V the bias voltage and N_d the donor concentration. The increase of the depletion layer will only increase the sensitivity in regions of incomplete absorption, i. e. only at high photon energies.

From the differences in the measured efficiencies using various monochromators and different experimental equipment, we estimate the uncertainty of our comparison with secondary standards to be $\pm 20\%$. This already includes the variations between different specimens of the same type of diode which are on the order of $\pm 10\%$.

The main contribution to the uncertainty is the uncertainty of the secondary standard diodes. The literature data for the photoyield of Au, on which our data are based in a large spectral region, differ by up to 60%. We therefore determined the efficiency of our Au-diode using an ionisation chamber in the spectral range between 70 and 800 eV (see appendix). Including the results of these investigations, we estimate the uncertainty of the secondary standards not to exceed $\pm 35\%$ in any spectral region. Therefore a total uncertainty of at most $\pm 40\%$ for the efficiencies and sensitivities of the investigated Schottky diodes can be assumed.

Independent from a secondary standard, an average value of the sensitivity for broad spectral ranges can be determined if the photodiode is irradiated with the undispersed synchrotron radiation of the electron storage ring BESSY, where the spectral photon flux can be calculated with an uncertainty of less than 2%²¹. With measurements at different electron energies different spectral region are emphasized. These measurements indicate that the values for the quantum efficiency and the sensitivity shown in Figs. 3 and 4 could be too low by more than 30% at photon energies above 200 eV. This is still within the uncertainties given above.

4. APPLICATIONS IN THE VUV AND SOFT X-RAY REGION

Both GaAsP- and GaP-diodes can be used through the entire spectral region of the UV, the VUV and the soft X-ray range, each type having its own advantages. GaP-Schottky-diodes show slightly larger differences in their efficiencies from specimen to specimen, especially at higher photon energies,

but the low efficiency of these diodes for visible light may sometimes be advantageous. In the spectral range above 1 keV, silicon diodes may be superior to GaAsP- and GaP-Schottky diodes^{22,23} even if they show severe degradation effects at lower photon energies. In this region a considerable part of the radiation penetrates through the rather thin depletion layer of the Schottky diodes investigated here, while it will still be absorbed in the depletion layer of diffusion type silicon diodes where the thickness of the space charge region is several μm .

An important field of application will be in optical spectroscopy in the VUV; e. g. in reflectometers and polarimeters. The main advantage of semiconductor diodes in this application is their excellent linearity and their insensitivity to polarization effects when used at normal incidence. For some applications the sensitive area of the diodes investigated here (4.6 mm \times 4.6 mm) may be too small. GaAsP diodes are commercially available with a sensitive area of 10 mm \times 10 mm, but it is our experience that the electric properties of these devices are not always reliable. We note further that the increase in efficiency with increasing photon energy emphasizes the contribution of higher harmonics in a spectrum.

Though the sensitivity of solid state detectors is much higher than those of photoemissive detectors, it is still much lower than the sensitivity of photomultipliers. Using low noise cable and an integration time of 1 s, the dark current and also the long term drift of the dark current is of the order of 20 fA. Assuming an average sensitivity of 0.15 A/W, this corresponds to a noise equivalent power NEP of 0.13 $\text{pW}/\sqrt{\text{Hz}}$ in agreement with measurements of Wilson and Lyall¹⁸ and with the manufacturers specification. Since reliable measurements require a photocurrent 10 times larger than the dark current, a radiation flux of about $2 \cdot 10^6$ photon/s at 20 eV and 6000 photons/s at 2 keV is needed if the quantum efficiency data from fig. 3 are used.

Thus Schottky diodes complement photomultipliers ideally which are indispensable in low level radiation measurements. There is even an overlapping region where multipliers can be used in a counting mode and solid state diodes in a photoamperic mode so that a direct efficiency determination of photomultipliers is possible.

5. CONCLUSIONS

For many applications Schottky diodes are superior to other detectors. They are particularly promising as calibrated standard detectors, because they are relatively insensitive to surface contaminations, show a high stability in intense VUV-radiation and possess a quantum efficiency up to 4 orders of magnitude higher than that of photoemissive detectors.

We have characterized semiconductor diodes by comparison with conventional detector standards. In the region between 70 eV and 800 eV an ionisation chamber has been used in addition. We have already initiated a program to calibrate Schottky diodes over the entire energy range using primary detector standards thus eliminating most of the problems presently connected with these transfer standards.

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APPENDIX

CALIBRATION OF OUR GOLD CATHODE IN THE PHOTON ENERGY RANGE FROM 70 TO 800 eV WITH AN IONISATION CHAMBER

In order to minimize the uncertainties associated to open photodiodes, we used an ionization chamber as a primary detector standard in our experiments on the Bumble-Bee monochromator.

The ionization chamber has been operated in a pressure range where the gas amplification by secondary processes is saturated. On the assumption that the energy E of the incident photons is distributed to electron-ion pairs of an average energy W , the ratio of the number of the absorbed photons $N_{\text{Phot,a}}$ and the number of ions N_{ion} is given by

$$\frac{N_{\text{Phot,a}}}{N_{\text{ion}}} = \frac{W}{E} \quad (3)$$

Therefore the number of incident photons $N_{\text{Phot,i}}$ can be calculated by

$$N_{\text{Phot,i}} = \frac{N_{\text{ion}} \cdot W}{E \cdot e^{-\sigma n l} \cdot (1 - e^{-\sigma n L})} \quad (4)$$

where σ is the cross section, n the particle density, l the length of the front region of the ionisation chamber where the ions are not collected, and L the length of the region where the ions are detected.

The measurements were made at eleven different photon energies between 71 and 800 eV with Argon and Xenon as filling gases. The required cross sections and W -values were taken from refs. 24 - 26. Although the W -values are measured with high-energy electrons, their application to photons in our energy range is justified by experiments with Xenon²⁷, which show that the high-energy electron W -value is applicable for photons of energies above twice the ionization threshold. Only in a small photon energy range above the onset of the 4d-ionisation of Xe this statement does not hold. Accordingly, the results in photon flux determined with the different gases deviate at the two measuring points at 98 and 117 eV. Thus, we rely at these points on the

argon results, while the mean of the values obtained with both gases is taken at all other energies. This is suitable as their deviation from each other is $\pm 15\%$ at worst with the only exception at 600 eV where the Xe result is lower than the Ar result by 21%. These differences are acceptable compared with the overall uncertainty of $\pm 14\%$ which arises primarily from the uncertainties in the W -values, the cross section values and the gas pressure measurements.

The quantum efficiency of the semiconductor diodes could in principle be obtained directly from the comparison to the ionisation chamber. For practical reasons, however, we used a gold diode as a secondary standard. Its efficiency is given in fig. 5 together with published data. The comparison leads to the conclusion that the actual efficiency of our cathode is reasonably well described by the data of refs. 11 and 12. Thus, these data are taken for the calculation of the presented efficiency and sensitivity values of the semiconductor diodes. However, the possible uncertainties in the photon energy range covered by the ionization chamber measurements can now be estimated from fig. 5. They are substantially reduced compared with the uncertainty of data obtained with uncalibrated reference diodes.

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E (eV)	Monochromator	Reference Diode
5 - 10	Seya-Namioka Monochromator (BESSY)	CsTe
10 - 40		Al ₂ O ₃
36 - 240	Toroidal Grating Monochromator (PTB at BESSY)	Au
70 - 1500	Plane Grating Monochromator "Bumble Bee" (HASYLAB)	Au
1000 - 3500	Double Crystal Monochromator (BESSY)	Au

Tab. 1: Monochromators and reference detectors used for the calibration of the Schottky diodes

FIGURE CAPTIONS

Fig. 1: Construction of a diffusion type Si-diode and a Schottky diode

Fig. 2: Stability of 3 different semiconductor diodes when irradiated with 10^{10} photons / (s mm²) at 124 eV

Fig. 3: Quantum efficiency of a GaAsP-Schottky diode, determined on different monochromators by comparison with photoemissive detectors (see table 1). The quantum efficiencies of the photoemissive reference diodes are also shown.

Fig. 4: Sensitivity of a GaP- and a GaAsP-Schottky diode without bias (——) and with a bias of 4.5 V (-----)

Fig. 5: Quantum efficiency of our gold reference cathode and literature data for the quantum efficiency of gold: —— refs. 11 and 12, ----- ref. 28

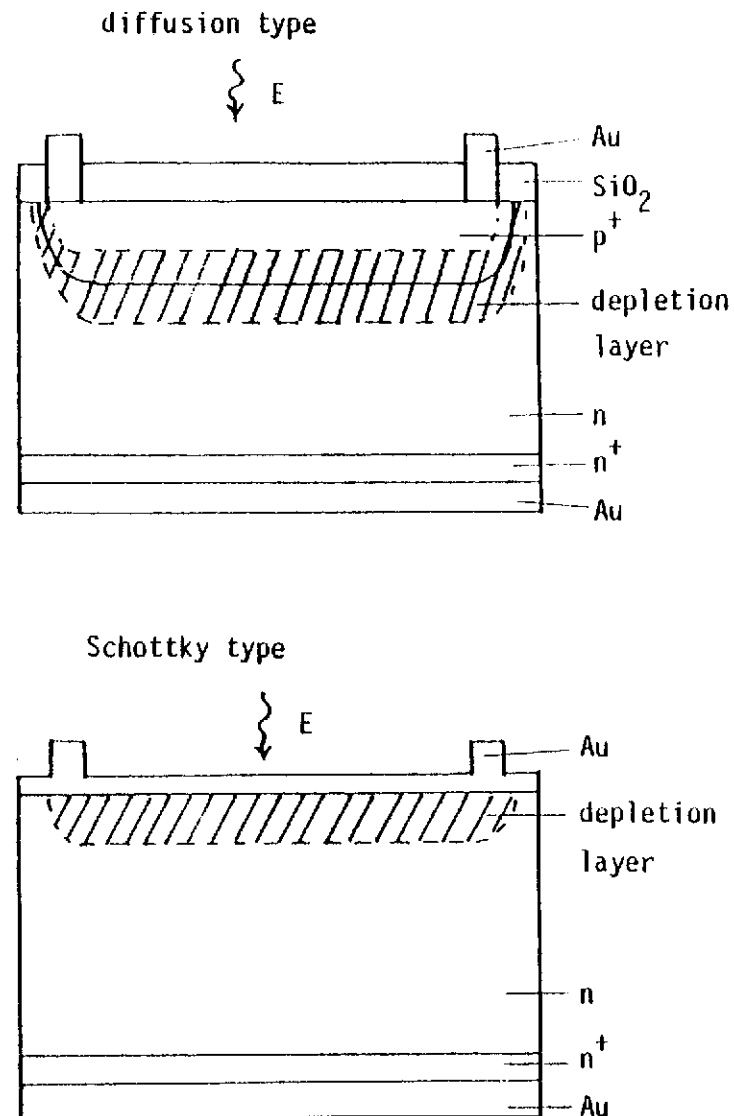


Fig. 1

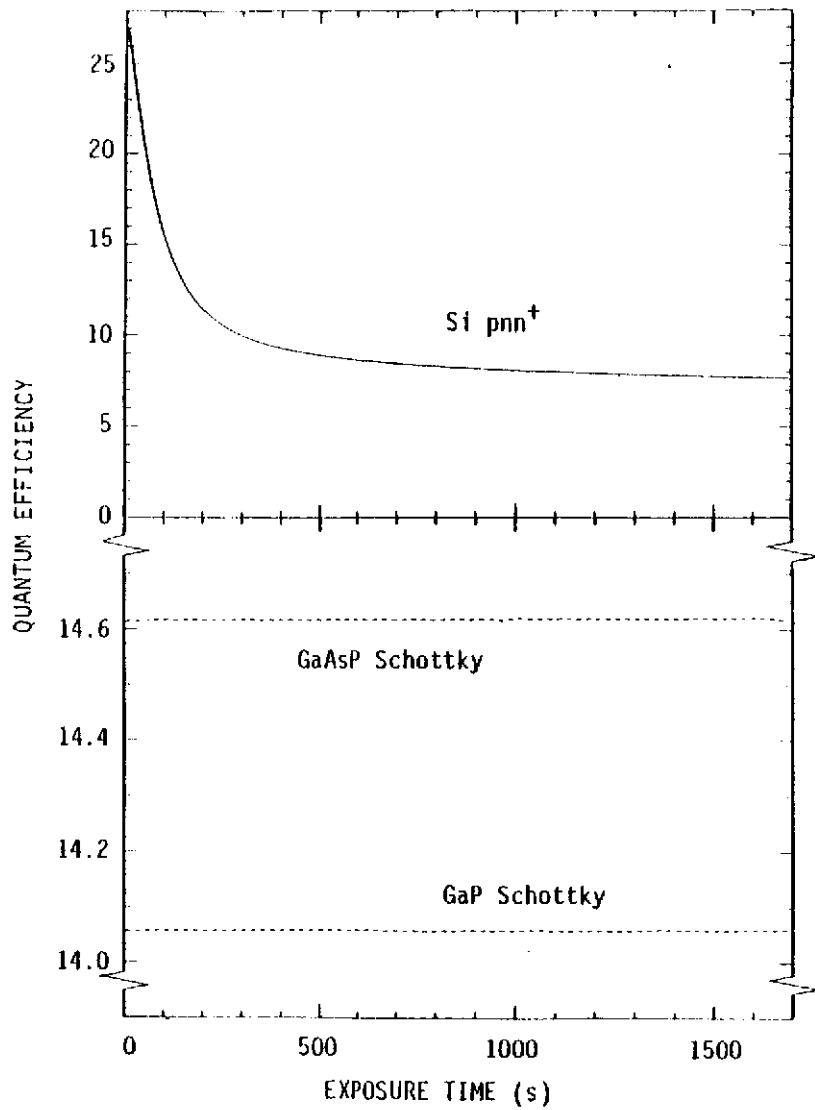


Fig. 2

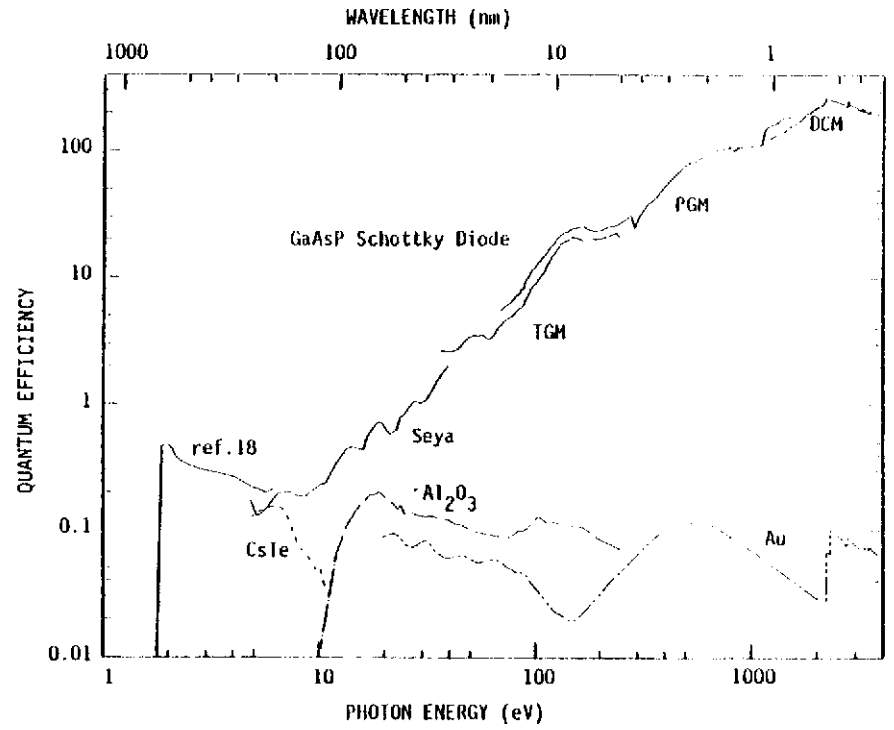


Fig. 3

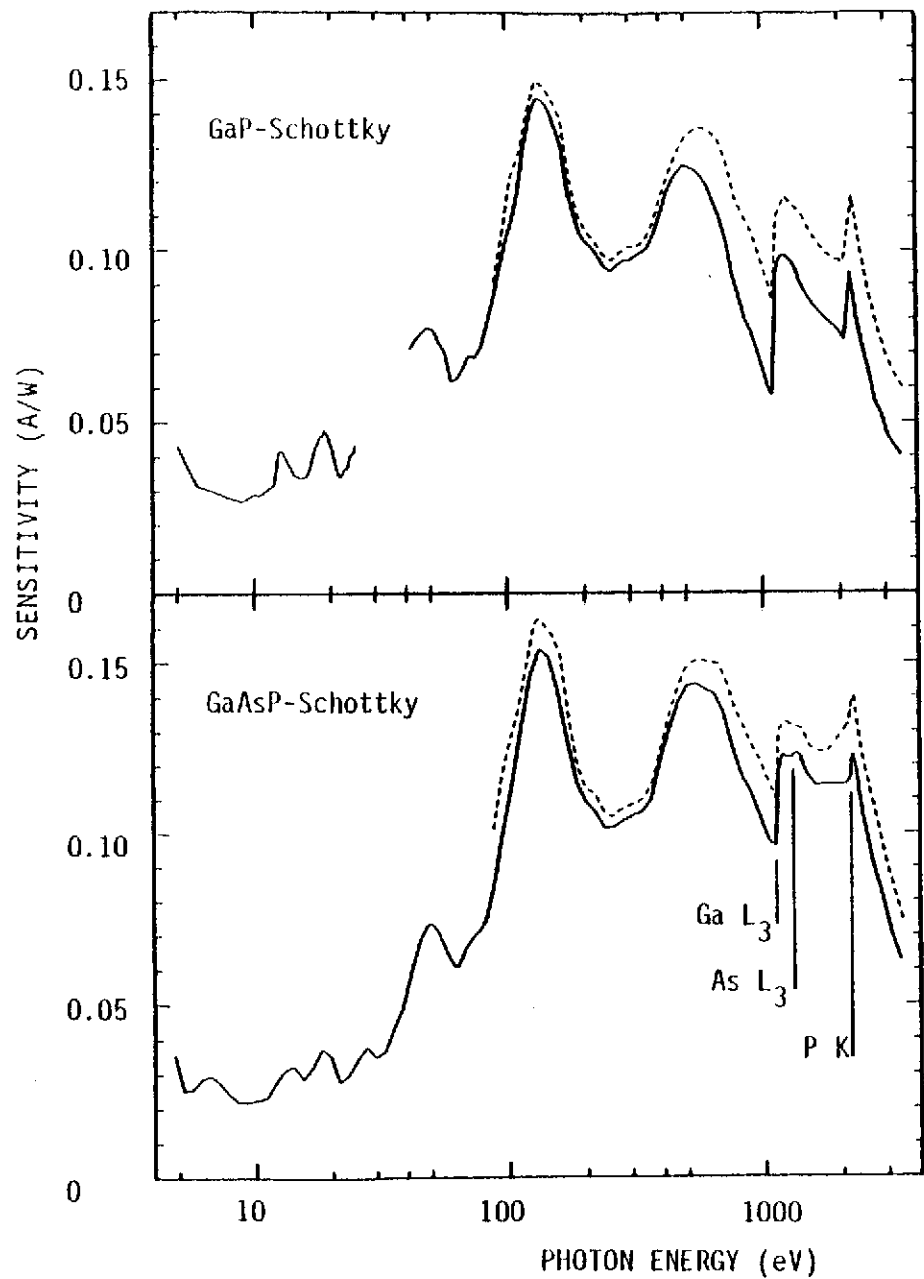


Fig. 4

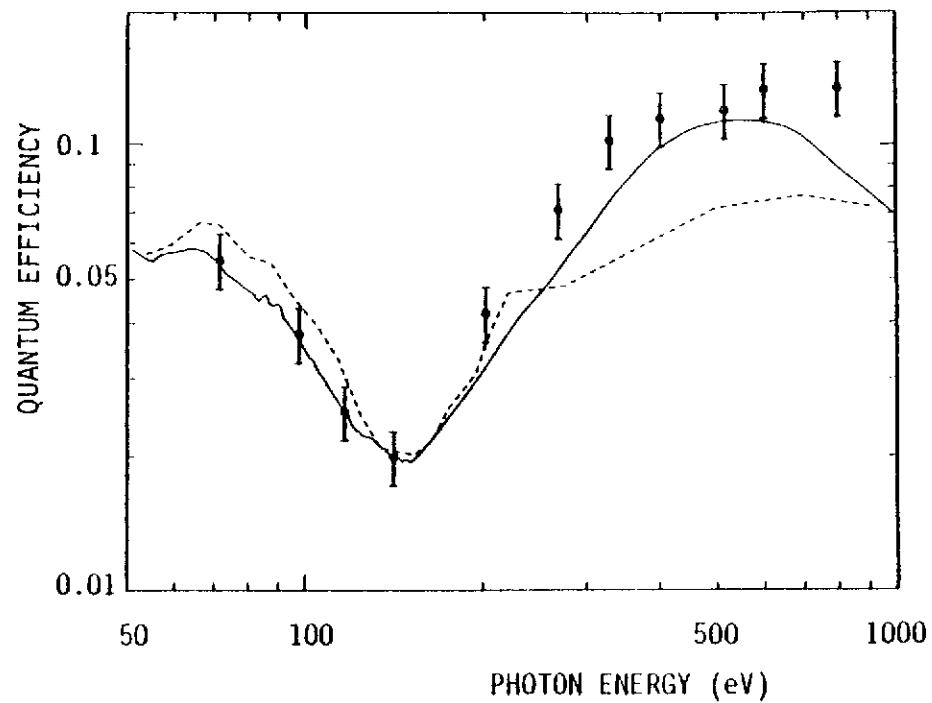


Fig. 5

