Optica Applicata VII/2, 1977

*Janusz M. Pawlikowski, Ewa Majchrowska, Bogdan Kochan**

Photovoltaic spectrum in $Si–Zn_3As_2$ heterojunctions**

Spectral characteristics of photovoltaic effect have been investigated in $(n)Si$-$(p)Zn_3As_2$ heterojunctions at 300 K. A mechanism of carriers excitation and a probable band model of heterojunction explaining the effects obtained have been proposed.

1. Introduction

The interest in semiconductor heterojunctions has grown considerably in the recent years. Such junctions may be applied as e.g. infrared sensitive image tubes (see e.g. [1, 2]) and semiconductor injection lasers [3].

Investigation on optical properties of heterojunctions, photoelectric properties included, provides essential information about their band model. Both the preparation and electric properties of $(n)Si$-$(n)Zn_3As_2$ heterojunctions have been described earlier in [4, 5].

In the present paper results of investigations on photovoltaic effect occurring on these heterojunctions, and the probable band model of heterojunction have been presented.

2. Experimental part

$Si–Zn_3As_2$ heterojunctions have been obtained by vacuum evaporation of a thin layer of Zn_3As_2 on monocrystalline silicone plate, in the way described in details in [4]. Spectral characteristics of photovoltaic effect have been measured in a standard system with a Zeiss monochromator, described e.g. in [6]. Resolving power of the system was not lower than 0.02 eV. Schematic representation of the examined structure of the heterojunction is given in fig. 1. The measurements of the photovoltaic effect have been performed in two variants: for radiation incident onto the Zn_3As_2 layer (about 0.5 μm thick), and that incident from the side of Si layer (about 0.5 mm thick).

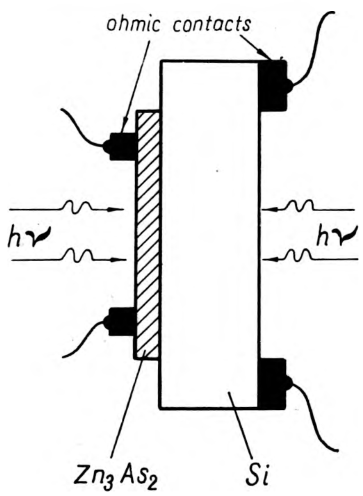


Fig. 1. Schematic set-up for the measurement of photovoltaic effect in $Si–Zn_3As_2$ heterojunction

3. Discussion of results

The examples of the results of measurements are presented in fig. 2a, b in the form of a dependence of normalized photoresponse on the energy of the falling photons. As it may be easily seen, they differ remarkably, depending upon the way in which the heterojunction was illuminated. To explain these differences and the character of the spectrum the distribution of photons flux responsible for this effect should be analyzed.

3.1. Photons incident onto the Zn_3As_2

If we denote the flux of photons by $I_0/h\nu$, then the flux penetrating into the layer will be $(1-R_1)I_0/h\nu$, where $R_1 = 0.3$–0.4 is the reflectivity from the Zn_3As_2 surface, given by the dispersion curve [7]. Due to absorption in the Zn_3As_2 layer the flux entering the heterojunction region is $(1-R_1)J_0/h\nu \exp(-\alpha_1 d_1)$, where d_1 denotes the thickness of the Zn_3As_2 layer, and α_1 is its absorption coefficient for the given photon energy. The value of α_1 near the absorption edge is of the order of 10^5 cm^{-1} [8], hence, the exponent factor in the spectral range of

* The authors are with Institute of Physics, Technical University of Wrocław, Wybrzeże Wyspiańskiego 27, 50-307 Wrocław, Poland.

** Work sponsored by Wrocław Technical University under contract 60/75, IM-116.

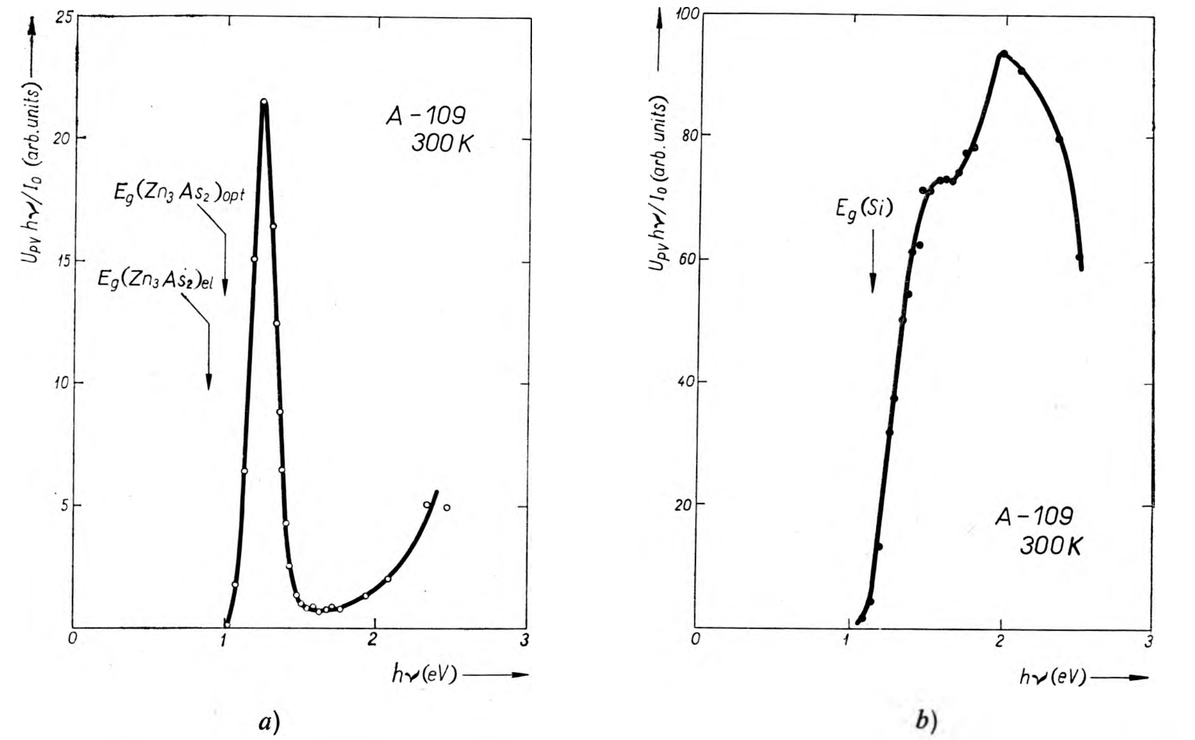
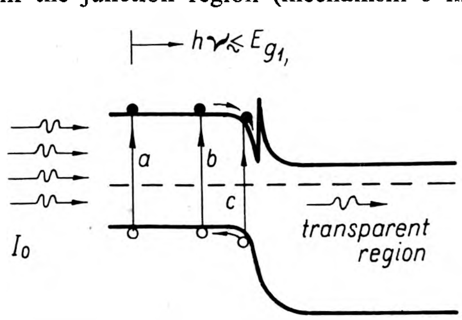


Fig. 2. Spectral characteristics of the heterojunctions examined

a) illumination incident onto the Zn_3As_2; b) illumination incident onto the Si, in form of a dependence of normalized photovoltage $U_{PV}(h_\nu/I_0)$ versus the energy of incident photons

our interest is $\alpha_1 d_1 = 5$. On the Zn_3As_2—Si interface the photons are additionally reflected from the Si surface, where reflectivity is R_2, thus only a negligeable part $(1-R_1)(1-R_2)I_0/h\nu\exp(-\alpha_1 d_1)$, amounting to about 0.1%, of the incident flux of photons with the energy $h\nu = E_{g1}$ enters the heterojunction in Si region. Schematic run of radiation, and energy distribution of photons are shown in fig. 3 a, b. In case of photons incident onto the Zn_3As_2 (fig. 3a) the part of them, for which $h\nu > E_{g1}$, will be absorbed in thin layer at the surface of Zn_3As_2 (mechanism *a* in fig. 3a). They, however, will not contribute to the signal of photoresponse, because of small difusion length*. On the other hand, the photons absorbed near the Si–Zn_3As_2 interface, at the distance not exceeding the carrier diffusion length in Zn_3As_2 (mechanism *b* in fig. 3a), and photons absorbed within the junction region (mechanism *c* in fig. 3a)



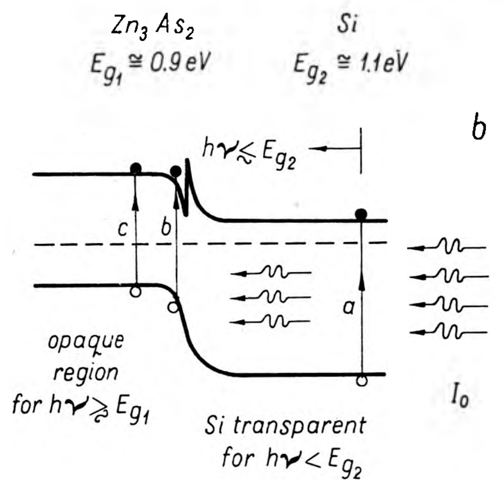


Fig. 3. Schematic distribution of incident photons and the mechanisms of carriers excitations

will contribute to the signal measured. Nevertheless, the number of free electron-hole pairs, generated according to the mechanisms *b* and *c* is not great, due to a strong absorption in the Zn_3As_2 layer (see above). That part of radiation (with energy $h\nu = E_{g1}$) which will leave the Zn_3As_2 region passes not absorbed by the Si region (since $E_{g2} > E_{g1}$).

Summing up, the photovoltaic effect in Si–Zn_3As_2 heterojunction, illuminated according to the variant shown in fig. 3a, is due to this part of total flux of photons with the energy $h\nu \simeq E_{g1}$, which enters the heterojunction region. It can be easily seen that for this way of illumination photoresponse will be selec-

*) The measurement results of both lifetime and diffusion length of carriers in thin Zn_3As_2 layer will be published elsewhere.

tive; photons of the energy $h\nu < E_{g1}$ will pass "unobserved" by heterojunction, whereas the photons with the energy $h\nu > E_{g1}$ will be absorbed intensly being still at the surface of the layer. The photoresponse spectrum (Fig. 2a) is in conformity with these expextations.

Considering the dominance of direct transitions within the region of the absorption edge in thin Zn_3As_2 layer [8], the number N of free electron-hole pairs (with a good approximation, proportional to the absorption coefficient) will depend on square root of the energy of incident photons

$$N \sim a \sim (h\nu - E_g)^{1/2}. \quad (1)$$

Thus, normalized photovoltage (for a low intensity of the incident radiation*) will be also proportional to $(h\nu)^{1/2}$

$$U_{PV}\frac{h\nu}{I_0} \sim (h\nu)^{1/2}. \quad (2)$$

The relation

$$U_{PV}\left(\frac{h\nu}{I_0}\right)^2 = f(h\nu)$$

for heterojunction illuminated from the side of Zn_3As_2 is shown in fig. 4a. The values of energy gap for thin layers of Zn_3As_2 estimated from optical [8] and electric [9] measurements are also marked in this figure. As it may be seen from fig. 4a the photoeffect threshold is in a fairly good agreement with the values of Zn_3As_2 energy gap (see also section 4. Final remarks), which confirms the analysis of the phenomenon investigated.

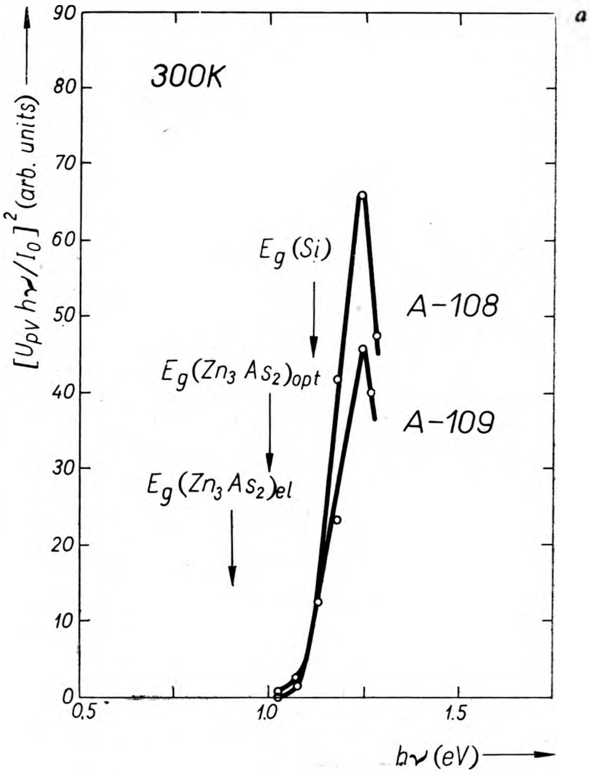
3.2. Photons incident onto the Si

This variant of heterojunction illumination is shown in fig. 3b. By the same way of reasoning, as in section 3.1, it may be easily shown that the heterojunction region is reached by photons with the energy $h\nu < E_{g2}$, the flux intensity being practically not reduced. On the other hand, within the heterojunction region and along the whole thickness of the Zn_3As_2 layer the photons with the energy $h\nu \simeq E_{g1}$ will be strongly absorbed (mechanisms *b* and *c* in fig. 3b). Photons with energies $h\nu < E_{g1}$, like in former case, will pass unabsorbed, thus they will not contribute to the photoeffect measured. Photons with the energy $h\nu \geqslant E_{g2}$ will be absorbed within the whole volume of Si, mostly at its surface (the factor

$$I_0/h\nu \exp(-\alpha_2 d_2)$$

---

*) This condition is well satisfied in standard monochromators, but should be thoroughly analyzed if the laser applied produces a beam of high energy density.



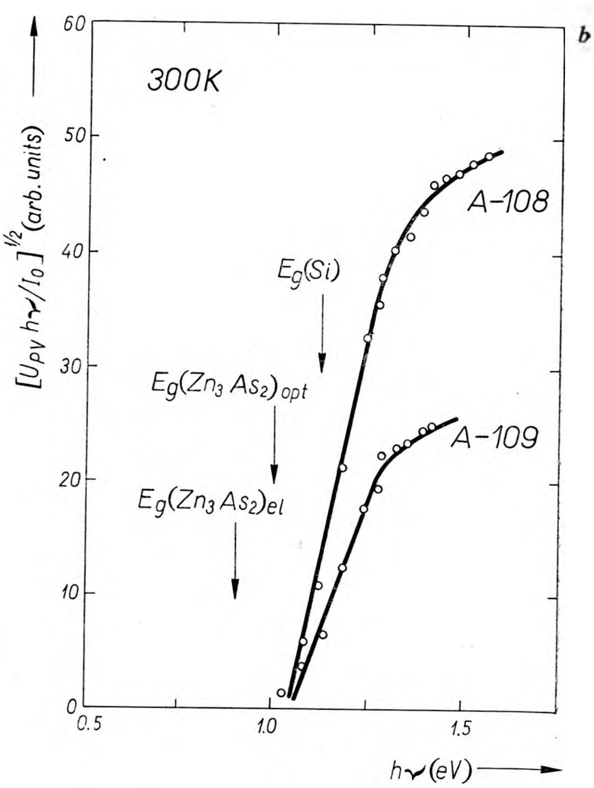


Fig. 4

a) $(U_{PV}(h\nu/I_0))^2$ versus energy of photons incident onto the Zn_3As_2 plate; b) $(U_{PV}(h\nu/I_0))^{1/2}$ versus energy of photons incident onto the Si layer quickly decreases with the thickness of Si plate). Because of the great diffusion length of the excess carriers in Si (of the order of the thickness of the measured Si plates [10]) they will diffuse into the region of heterojunction barrier, thus contributing to the photovoltage measured.

Thus, it should be expected (at the illumination from the Si side), that in this case the spectral characteristics will be more diffused than for the case discussed in 3.1. This diffusion will be due to superposition of the effects resulting from photoexcitation of carriers in Zn_3As_2 region (for $h\nu \cong E_{g1}$), in heterojunction region (for $E_{g1} < h\nu < E_{g2}$), as well as in Si region, both within its volume and at the surface (for $h\nu \geqslant E_{g2}$).

In case of Zn_3As_2 the transitions are directed and the relations (1) and (2) ar: true, while in silicon the optical transitions are indirect, with absorption or emission of phonon of the energy E_p, for which

$$a \sim (h\nu - E_{g2} \pm E_p)^2. \tag{3}$$

Thus, in this case normalized photoresponse will be proportional to the square of photons energy

$$U_{PV}\frac{h\nu}{I_0} \sim (h\nu)^2. \tag{4}$$

The relation

$$\left(U_{PV}\frac{h\nu}{I_0}\right)^{1/2} f = (h\nu)^{1/2}$$

for heterojunctions shown in fig. 4a, illuminated from the Si side, is presented in fig. 4b. In this same figure the value of energy gap of Si, $E_{g2} = 1.12$ eV (at 300 K) is also merked. It follows from this figure that the spectral characteristics is in a qualitative agreement with our expectations.

3.3. Proposition of heterojunction band model

The position of low energy longwave length edge of photovoltaic effect determined experimentally is of an essential importance for the identification of band model of the examined heterojunctions. For both the variants of illumination this position is similar, and occurs for the energy $h\nu = 1.000-1.10$ eV (see fig. 4a, b). This is particularly important in the case of illumination from the side of silicon, which is practically transparent for $h\nu < E_{g2}$. At such an illumination the photo-generation processes in semiconductor with a narrower energy gap provide a distinct or dominant cantribution to the photovoltage produced [11]. In this case longwave edge of the effect is determined chiefly by the transitions of electrons in Zn_3As_2 in the vicinity of the heterojunction interface.

Now we must explain the value of longwave edge the effect of which is somewhat higher than the value of energy gap in Zn_3As_2 (estimated from electric measurements, $E_{g1} = 0.9$ eV [9], and assumed for the model of heterojunction, proposed in papers [4, 5]), being however, close to the value of energy gap, estimated from optical measurements [8]. In the model from [4, 5] the value of the conduction band edge break has been also determined in boundary region, and denoted in fig. 5 as ΔV_c, ($\Delta V_c = 0.18$–0.2 eV at 300 K). The value of surface density of

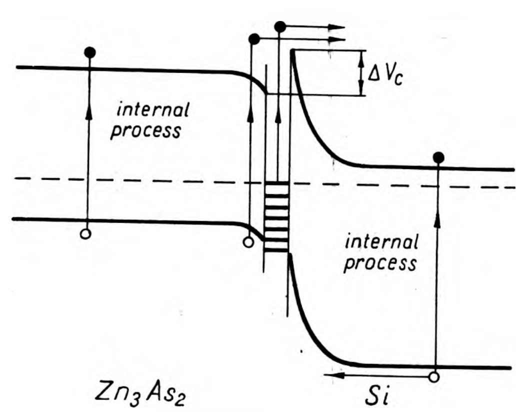


Fig. 5. Band model of Si–Zn_3As_2 heterojunction and mechanisms of carriers generation

energy states on the junction interface (dependent on the heterojunction technology) has been also determined; it amounts to about 3×10^{16} m^{-2} for the technology generating the greatest density of these states [5]. For the technology applied in the present work the estimated density of the surface states is slightly lower than 10^{16} m^{-2}.

Thus, in the model of heterojunction, which is to explain the results obtained, the presence of interface states (lying in energy gap) should be taken into consideration. The model suggested is shown in fig. 5; the interface states lying on, and below the Fermi level are marked (surface states above Fermi level being empty their presence may be neglected in the analysis).

The position of longwave photoeffect edge can be now explained by means of two independent effects (see fig. 5):

1) electron-hole pair in Zn_3As_2 near the interface generated by the photon with the energy

$$h\nu = E_{g1} + \Delta V_c \tag{5}$$

and transition of electron over the barrier into the region of silicon;

2) photoexcitation of electron from surface state on the Fermi level by the photon with the energy

$$h\nu = E_{g1} - E_F + \Delta V_c \tag{6}$$

and transition of the electron over the barrier. The second effect seems to be less probable, since it requires a simultaneous removal of the hole from this state, e.g. by photoexcitation, thermal emission or tunneling [11]. Nevertheless, while determining quantitatively the position of the threshold the two values will be used.

The application of the E_g-value, estimated from optical measurements ($E_{g1} = 1.0$ eV), to the description on the mechanism 1) gives the value of photothreshold $h\nu = 1.18$–1.20 eV, which is distincly higher than that stated experimentally. A fairly good agreement is, however, obtained by inserting this value to the equation (6), since then $h\nu = 0.93$–0.95 eV. Analogically, the value estimated from electric measurements $E_{g1} = 0.9$ eV, inserted to the equation (5), is in a relatively good agreement with the experiment, $h\nu = 1.08$–1.1 eV, whereas applied to the equation (6) it is lower, $h\nu = 0.08$–0.85 eV.

The influence of Franz-Keldysh effect [12, 13] on the longwave-threshold value of the effect cannot be excluded either. Because of a great difference in impurities concentration practically the entire 0.6 μm thick interface region (bending of the bands) falls to silicon. Thus within the barrier the value of electric field intensity will be equal to about 10^6V/m [4], this value being sufficiently high for the occurrence of the Franz-Keldysh effect. Thus, there is a probability of the electron photoemission from Zn_3As_2 valence band on the level lying in energy gap, and then its tunneling to silicon. Considering, however, the value of field intensity and barrier width in Si, it seems that this process will not contribute significantly to the photovoltage measured.

4. Final remarks

The heterojunctions examined have been illuminated from the Si and Zn_3As_2 sides. The differences of the obtained spectral characteristics can be explained qualitatively by the mode presented schematically in fig. 3. Since — on the one hand — attenuation of radiation in Si is equal to or greater than in Zn_3As_2 for extreme values of photons energy (for $h\nu < E_{g1} < E_{g2}$ we have $\alpha_1 d_1\,(Zn_3As_2) \cong 0.1 = \alpha_2 d_2(\mathrm{Si}) \cong 0.1$ and for $h\nu > E_{g2} > E_{g1}$ we have $\alpha_1 d_1 \cong 10 < \alpha_2 d_2 = 500$), and — on the other hand — the diffusion length of excess carriers in silicon is much longer than in Zn_3As_2, hence a selective character of the photovoltaic-effect curve for illumination from the side of Zn_3As_2, as well as wind-band character of the curve, extended towards higher energy at the illumination from the side of Si, are quite understandable.

Of the two internal generation processes, presented in fig. 5, the process occurring in silicon contributes significantly to the voltage measured, because of a relatively long diffusion lenght of excess carriers. This, as well as the possibility of the generation of electron-hole pairs by hot electrons (generated by photons with the energy $h\nu > E_{g2}$) explain broad photovoltaic spectrum, extended up to the energy of 3 eV.

Summing up, because of a slight difference in the values of energy gap of the semiconductor used, and due to the existence of energy states of heterojunction interface, it cannot be decided actually which of the two photoemission processes, shown in fig. 5, prevails.

*

* *

The authors are greatly indebted to J. Dubowski for his participation in discussion of the results. One of us (J. M. Pawlikowski) expresses his gratitude to Dr. C. Van Opdorp (Philips Res. Lab., Eindhoven) for making available the results of his works.

Фотовольтаитный спектр в гетеросоединениях $Si-Zn_3As_2$

Исследовались спектральные характеристики фотовольтаичного эффекта в гетеропереходах $(n)\,\mathrm{Si} = (p)Zn_3As_2$ в температуре 300 K. Предложили механизм экситации носителей, а также возможную зонную модель гетеросоединения, объясняющую полученные результаты.

References

[1] Kruse P. W., Pribble F. C., Schultze R. G., J. Appl. Phys. **38**, 1967, p. 1718.
[2] Van Ruyven L. J., Williams E. P., Solid State Electron. **10**, 1967, p. 1159.
[3] Rediker R. H., Phys. Today **18**, 1965, p. 42.
[4] Pawlikowski J. M., Kochan B., Dubowski J., Materials Science **2**, 1976, p. 15.
[5] Dubowski J., Kochan B., Pawlikowski J. M., Materials Science **2**, 1976, p. 89.
[6] Becla P., Dudziak E., Pawlikowski J. M., Opt. Appl. **4**, 1974, p. 3.
[7] Żdanowicz W., Pawlikowski J. M., Acta Phys. Pol. **A38**, 1970, p. 11.
[8] Pawlikowski J. M., Borkowska T., Opt. Appl. **4**, 1974, p. 31.
[9] Pawlikowski J. M., Becla P., Acta Phys. Pol. **A47**, 1975, p. 121.
[10] Hogarth C. A., Proc. Phys. Soc. **B69**, 1956, p. 761.
[11] Van Opdorp C., Inter. Conf. on Phys. Chem. Semicond. Heterojunct. Layer Structure, Budapest, October 1970.
[12] Franz W., Z. Naturforsch. **13a**, 1958, p. 484.
[13] Keldysh L. V., Sov. Phys.-JETP **7**, 1958, p. 788.

Received November 22, 1976