phys. stat. sol. 20, 255 (1967)

Subject classification: 14.3.2; 16; 22.1.2; 22.4.1

Institut für Technische Elektronik der Technischen Hochschule München

Electrical and Photovoltaic Properties of PbS–Si Heterodiodes

By

H. SIGMUND and K. BERCHTOLD

The electrical and photo-electrical properties of PbS–Si heterodiodes are investigated. The PbS films are grown on Si by a water-solution reaction at room temperature. The forward and reverse characteristic is similar to that for other heterojunctions (recombination-tunneling mechanism). The spectral response is in the wavelength range 1 to 3 μm at room temperature. The sensibility in the PbS peak is about 6×10^3 V/W.

Es wird über PbS–Si-Heterodioden berichtet, bei denen die PbS-Schicht aus wäßriger Lösung auf Si-Kristalle bei Zimmertemperatur niedergeschlagen wurde. Die elektrischen und photoelektrischen Eigenschaften dieser Dioden werden gezeigt. Das Durchlaß- und Sperrverhalten ist mit anderen Heteroübergängen vergleichbar (Rekombinations-Tunnelmechanismus). Die spektrale Empfindlichkeit erstreckt sich von 1 bis 3 μm bei Zimmertemperatur, mit einer Empfindlichkeit im PbS-Maximum von ca. 6×10^3 V/W.

1. Introduction

Several heterojunctions between Ge, Si, and $A_{III}B_V$ semiconductors have already been investigated intensively. For instance, Ruth et al. [1], Marinace [2], Anderson [3], and Rediker et al. [4] reported on heterojunctions with GaAs. Shewchun and Wei [5, 6], Oldham and Milnes [7], Hampshire and Wright [8], Yawata and Anderson [9], and Donnelly and Milnes [10] discussed Ge–Si heterojunctions. However, there is little information about heterojunctions with PbS as partner. Davis and Norr [11] were the first who reported on epitaxial films of PbS on a Ge substrate. PbS heterojunctions are especially of interest in regard to their spectral response. In addition, the preparation of the diodes by depositing a semiconducting film from a water solution of reacting chemicals at room temperature is a more simple method than alloy processes and methods of epitaxy from vapour phase [12] as well. Davis and Norr [11] obtained single-crystalline PbS films on Ge substrates. The difference of the lattice constants in this case is about 5.4%. The lattice mismatch for PbS–Si, however, is approximately 9%. Therefore, many lattice defects at the interface of the junction (density of dislocations about $7 \times 10^{15}/\text{cm}^2$ [12]) are introduced or even a polycrystalline growth of PbS on the Si substrate may be possible.

2. Structure and Preparation of the Diodes

The PbS layers were deposited on n-type silicon (resistivity about 4 Ω cm, surface orientation [111]). Prior to depositing PbS gold-plated molybden rings have been evaporated (see Fig. 1a). The opposite Si-surface was polished mechanically and chemically (CP4). A modification of the structure in Fig. 1a

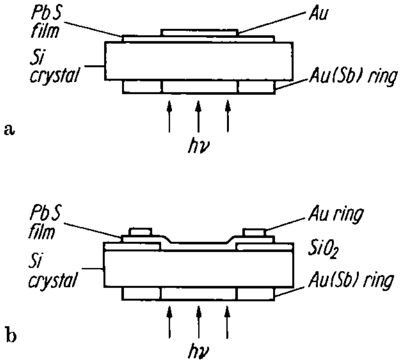


Fig. 1. Structure of the PbS-Si heterodiodes a) without oxide window, b) with oxide window

is shown in Fig. 1b. The oxide window was fabricated by planar technique. The ohmic contact on PbS was achieved by evaporated gold films in both cases.

In order to grow the PbS layers, the crystals were mounted on a metallic support and submerged into a solution consisting of 2 parts 0.39 molar thiourea, 1 part 0.33 molar lead acetate and 0.003 parts 50% hydracine hydrate. After 3 min 0.3 parts 17.5 molar NaOH have been added. The reaction lasted about five minutes. Then the samples were rinsed with distilled water and methanol.

3. Structure of the PbS Films

The PbS film structure was investigated by transmission electron diffraction. In order to remove the PbS films from the substrate the crystals were submerged shortly in a 1 molar HCl solution. A typical transmission pattern is shown in Fig. 2. The apparent Debye-Scherrer rings indicate a polycrystalline structure

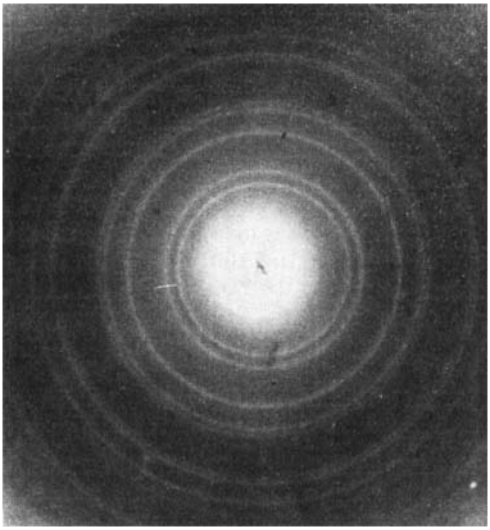


Fig. 2. Electron diffraction pattern of a PbS layer

of the PbS films. Therefore, the corresponding films of the PbS–Si heterodiodes will also be of polycrystalline material, provided that during the preparation process the original structure had not been modified significantly.

4. Electrical Properties

The *U–I* characteristic of the heterodiodes in the dark and under illumination are shown in Fig. 3. If the Si side of the heterojunction is positive biased, the reverse characteristic of the diodes is observed. The reverse current below 1 V bias is proportional to U^n, with n varying between 1 and 0.5. For larger bias the current is proportional U; for bias exceeding about 30 V strong irreversible changes in the *U–I* characteristic are observed. Forward characteristics are shown in more detail in Fig. 4. All characteristics change their slopes at about 0.1 V. According to the theories of Riben [13] and Donnelly [14] it is supposed, that the forward current below this point is a pure recombination current, and above this point it is mainly a tunnelling current. The recombination current is proportional to exp $(e\,U/n\,kT)$, n being a characteristic constant varying between 1.3 and 2 according to Fig. 4. On the other hand, the temperature-dependent tunnelling current is proportional to exp $(A\,U)$, where the constant A ranges between 20 and 30 V^{-1}. Further measurements confirmed the independence on temperature of the constant A.

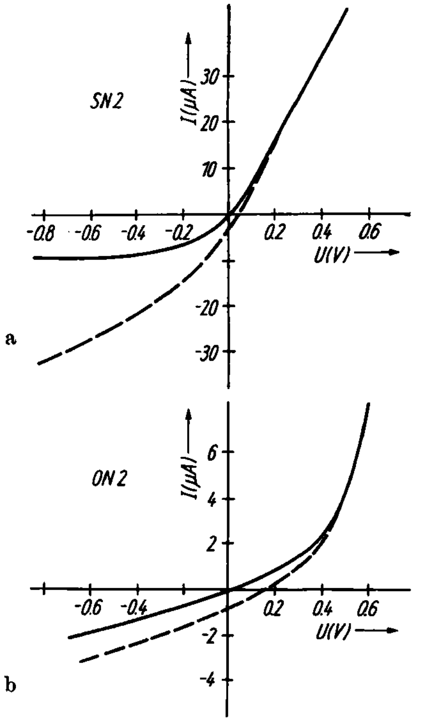


Fig. 3. *U–I* characteristics of two PbS-Si heterodiodes without (——) and with (- - -) illumination at room temperature

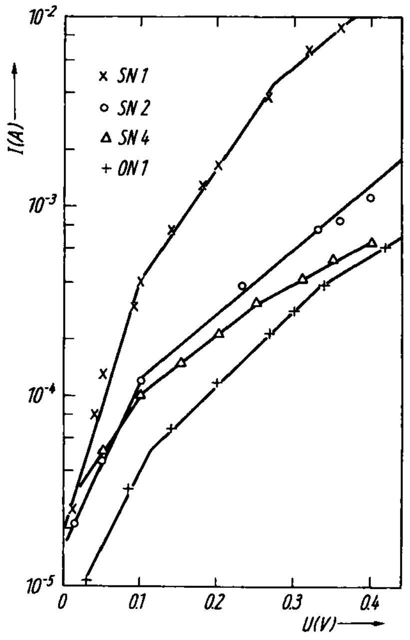
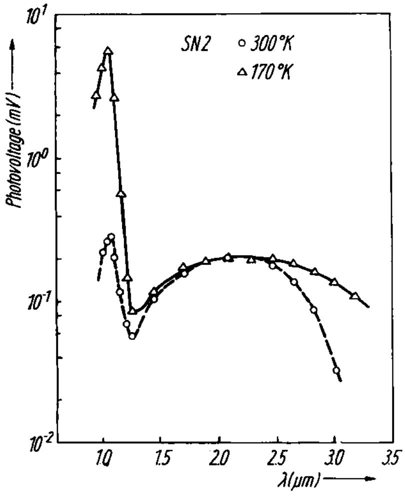


Fig. 4. Forward characteristics of different PbS-Si heterodiodes at room temperature in semilogarithmic plot



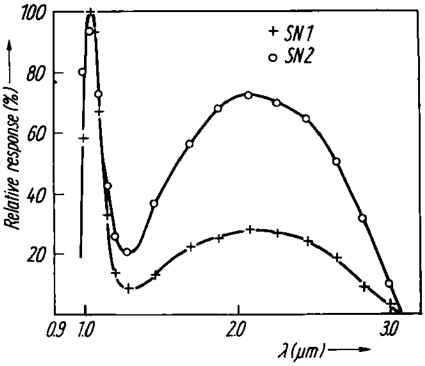


Fig. 6. Relative spectral response of two heterodiodes at room temperature. The response refers to equal irradiated power

Fig. 5. Spectral response of a typical PbS-Si heterodiode at 300 and 170 °K. The response refers to equal irradiated power

5. Photovoltaic Properties

The spectral response of the heterojunctions (Fig. 5 and 6) shows the "window effect" which is caused by the different band gaps. The peak of the photovoltage at 1 μm (Si absorption) depends on the temperature in contrast to the peak at 2 μm (PbS absorption, see Fig. 7). The temperature coefficient of the Si-photopeak in the measured temperature range is approximately 1.6% per deg. At low temperatures (170 °K) the known extension of the spectral response of PbS to longer wavelengths has been observed (Fig. 5).

The absolute sensitivity of several diodes at room temperature was measured. The radiant power of a black body at 1000 °C incident to the sensitive area was 1.5×10^{-5} W. The heterodiodes exhibit a sensitivity of $S_{\text{black, 1000 °C}} = 200$ V/W. The spectral response at 1 μm is $S_{\lambda=1\,\mu\text{m}} = 0.8$ to 1×10^4 V/W; at 2.4 μm $S_{\lambda=2.4\,\mu\text{m}} = 0.5$ to 0.7×10^4 V/W. The photovoltage is up to 20 mV proportional to the incident power.

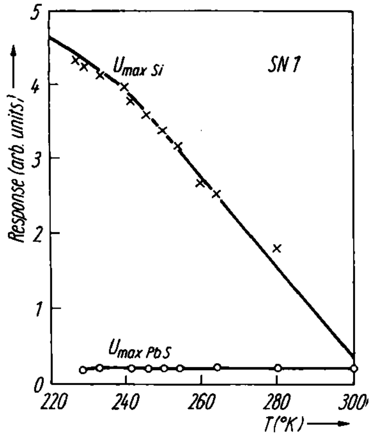


Fig. 7. Temperature dependence of the photovoltage at 1 μm (Si absorption) and 2 μm (PbS absorption)

6. Discussion

According to the electron diffraction patterns, the PbS layers on the Si substrate exhibit obviously polycrystalline structure. However, due to the experimental results concerning the U–I characteristic of the diodes, the heterojunction model after Riben [13] and Donnelly [14] can be applied. Hence, the forward current below 0.1 V is a recombination current, for larger bias it is mainly a tunnelling current. The so-called "power-law", however, for the reverse current could not be confirmed.

Thermoelectric measurements indicate p-conduction of the deposited PbS films. Therefore, the device can be regarded as a p-PbS–n-Si heterojunction. The measurements of spectral response and sensitivity promise an application of this device as an *IR*-detector in the wavelength range from 1 to 4 μm. Preliminary measurements indicate a time constant of several μs.

Acknowledgements

We are indebted to Dr. I. Ruge and Dr. W. Harth for stimulating discussions. We also would like to thank Mrs. H. Leitermann for technical assistance.

References

[1] R. Ruth, J. C. Marinace, and W. Dunlap, J. appl. Phys. **31**, 995 (1960).
[2] J. C. Marinace, IBM J. Res. Developm. **4**, 248 (1960).
[3] R. L. Anderson, Solid State Electronics **5**, 341 (1962).
[4] R. H. Rediker, S. Stopek, and J. H. Ward, Solid State Electronics **7**, 621 (1964).
[5] L. Y. Wei and J. Shewchun, Proc. IEEE **51**, 946 (1963).
[6] J. Shewchun and L. Y. Wei, J. Electrochem. Soc. **111**, 1145 (1964).
[7] W. G. Oldham and A. G. Milnes, Solid State Electronics **7**, 153 (1964).
[8] M. J. Hampshire and G. T. Wright, Brit. J. appl. Phys. **15**, 1331 (1964).
[9] S. Yawata and R. L. Anderson, phys. stat. sol. **12**, 297 (1965).
[10] J. P. Donnelly and A. G. Milnes, Solid State Electronics **9**, 174 (1966).
[11] J. L. Davis and M. K. Norr, J. appl. Phys. **37**, 1670 (1966).
[12] J. R. Dale, phys. stat. sol. **16**, 351 (1966).
[13] A. Riben, Thesis, Carnegie Institute of Technology, Febr. 1965.
[14] J. P. Donnelly, U.S. Army Research, Contract DA-31-124-ARO (D)-131.

(Received December 20, 1966)