Chalcogenide Materials for Solar Energy Conversion

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Abstract: The problem of electrical energy storage can possibly be solved with the help of electrochemical solar cells, which are suitable to generate either electrical energy or hydrogen gas under special conditions. The greatest problem of the electrochemical solar cell technology is to find novel materials which have appropriate properties for electrochemical energy conversion. In this work Cd_4GeSe_6, a novel material for electrochemical solar cells, will be presented.

1 Introduction

Solar cell technology is a very developed area of microelectronics; however, there are still some problems under research. One of the greatest problems in solar cell applications is the storage of electrical energy. This problem can possibly be solved with the help of electrochemical solar cells, which are suitable to generate either electrical energy or hydrogen under special conditions [1]. The technology of electrochemical solar cells has some technical and scientific problems. One such problem is photocorrosion, which occurs at the electrolyte–semiconductor interface. Photocorrosion damages the semiconductor electrode during the operation of the solar cell. This problem can be solved by avoiding the photocorrosion effect with the help of dye sensitized nanocrystalline TiO_2 material. The band diagram of the dyesensitized photoelectrochemical solar cell is shown in Fig. 1. A possible direction of this research is the search for novel materials with appropriate properties for electrochemical applications. One of the important groups of such semiconductor compounds is the chalcogenides such as Cd_4GeSe_6.

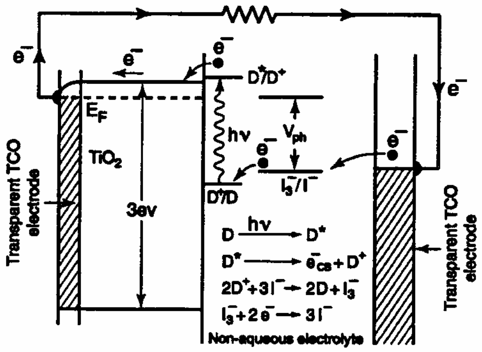

Figure. 1. The band diagram of the dyesensitized photoelectrochemical solar cell

In this work Cd_4GeSe_6, a novel material for electrochemical solar cells, will be presented. The properties of this material will be investigated, which has been scarcely done before, and that is why these properties are not known in detail. Cd_4GeSe_6 belongs to the agryrodite family, of which lattice parameters were determined [2]. The band gap and type of band transition was determined by absorption and the I-V characteristics was determined by photoelectrochemical method [3]. Furthermore it was found that this material shows very good resistivity against photocorrosion [4]. The knowledge of the electrical parameters of the Cd_4GeSe_6–electrolyte junction is very important for solar cell applications. It was also determined in this work. The properties of the Cd_4GeSe_6 crystal–electrolyte junction are investigated with impedance analysis. The evaluation of the measured data was carried out with the help of a computer program developed by us in Pascal language. We used an equivalent circuit with physical meanings, this circuit was appropriate for the calculations [5].

2 The Chalcogenide Material

A possible direction of semiconductor research is the search for novel materials with appropriate properties for different applications. One of the important groups of such semiconductor compounds is the group of chalcogenides, a well-known example of binary compounds. They are good photoconductors and have high absorption coefficient. Material properties can be improved and modified by forming ternary, quaternary etc. compounds of the above. Ternary chalcogenid materials, such as Cd_4GeSe_6, were synthesized in which new covalent chemical bonds appeared. Due to these covalent bonds these materials show higher resistance against corrosion. This novel property in itself makes novel applications, such as photoelectrochemical energy conversion electrode, possible.

In this work the properties of Cd_4GeSe_6 are investigated which are until now scarcely studied and therefore not known in details. The existing data in the literature differ over a wide range even for fundamental material parameters such as lattice parameters, band gap or type of band transition. This material belongs to the agrirodite family, which belongs to the monoclinic crystal class. The structure of chemically analogous compounds was investigated earlier [6]. The optical parameters of Cd_4GeSe_6 were scarcely studied possibly because of the difficulty of making larger pieces of single crystal.

The synthesis of Cd_4GeSe_6 crystal can be carried out from chalcogenide and dichalcogenide sources. The crystallizing period is several weeks long. The Cd_4GeSe_6 is a stable crystal and keeps its stability even at high temperatures under normal atmospheric conditions.

3 Photoelectrochemical Investigation

The band gap was determined by absorption [3] and photoelectrochemical [7] methods and was found to be 1.7 and 1.75 eV respectively. A further reference [8] gives 1.5 eV band gap and indirect band transition. Ref. [9] gives 1.9 eV for band gap from photoluminescence measurement at 10 K. These strongly different photoelectrochemical and photoluminescence results are refined in Ref. [3].

The impedance measurements were performed in an electrochemical cell under potentiostatic control. The electrolytes were 0.05 M H_2SO_4 and solution. The impedance analysis was carried out with the perturbation of some mV. The modeling of an electrolyte– semiconductor junction is a difficult problem because the values of the circuit elements exhibited frequency dependence. In this work we determined the proper values of equivalent circuit components with their physical meaning for the transfer function of the junction. The parameters of the equivalent circuit are very important to know for device applications. A simple equivalent circuit with physical meaning was appropriate for the calculation [5]. It contains three parallel branches, one branch is a resistance R_1, the second branch is a swinging circuit (R_2C_2) and the third branch is a capacitor (C_3).

The evaluation of the measured data was carried out with the help of a computer program developed by us in Turbo Pascal language. The transfer function of the equivalent circuit has three solutions (one zero and two poles). In the first step these three roots were fitted in the same time with the help of the least square method. The minimum of the error is determined with the help of gradient method, until the error becomes less than 1 Hz. The value of the constant in the transfer function was determined from the amplitude diagram with similar method [10]. The R_1 resistance represents the charge transfer that is the electrochemical reaction at the interface. The value ranges from 6.2 to 7.1 $k\Omega/mm^2$. R_2 and C_2 represent the surface levels and deep centers where the values range between 0.6 and 1.6 $k\Omega$

/mm^2 and between 5.3 and 7.6 nF/mm^2, respectively. The element C_3 means the space charge capacitance and its value is between 0.62 and 0.78 nF/mm^2 without bias voltage. The space charge capacitance shows a little larger value in KOH then in H_2SO_4 solution. Measured and fitted amplitude and phase diagrams of the junction are shown in Fig. 2.

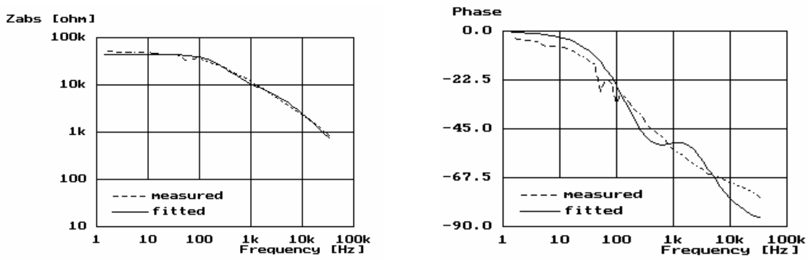

Figure 2. The amplitude and phase diagrams of the Cd_4GeSe_6 and 0.05 M H_2SO_4.

The junction of electrolyte–Cd_4GeSe_6 crystal was investigated with impedance analysis. We set-up an equivalent circuit of this junction. The electrical parameters of the junction were determined which are very important to know for device applications. The space charge capacitance was found to be about 0.9 nF/mm^2. The charge transfer resistance was about 5 kΩ/mm^2. The values of the elements of the RC circuit which represent the surface levels are 1.7 kΩ/mm^2 and 1.5 nF/mm^2, respectively. This model describes the electrical behavior of the junction in the whole investigated frequency range. Furthermore the surface morphology of Cd_4GeSe_6 crystal was investigated after electrochemical treatment [4].

References

[1] Á. Nemcsics: Solar Cells and their Developing Perspective; Academic Publisher, Budapest 2001

[2] K.-F. Hesse, M. Czank and Á. Nemcsics; Z. Kristallogr. 216**,** (2000) 14

[3] I. Kovách, Á. Nemcsics and Z. Lábadi; Inorganic Materials, 39 (2003) 108

[4] Á. Nemcsics; to be published

[5] Á. Nemcsics; phys. stat. sol. (a), 173, (1999) 405

[6] P. Quenez and O. Gorchov; J. Cryst. Growth 26 (1974) 55

[7] W. F. Kuhs, R. Nitsche, K. Scheunemann; Mater. Res. Bull. 14 (1979) 241

[8] B. von Krebs, J. Mandt; Z. Anorg. Allg. Chem. 388 (1972) 193

[9] P. Quenez, A. Maurer; J. Phys. 36 (1975) 83

[10] P. Turmezei, Á. Nemcsics; phys. Stat. Sol. (c) 0 (2003) 967