

CHALCOGENIDE MATERIALS FOR ELECTROCHEMICAL SOLAR CELLS

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SUMMARY

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.

Keywords: Electrochemical solar cell, chalcogenide material

1. INTRODUCTION

Solar cell technology is a well-developed area of electronics; however, there are still some unsolved issues under research. Theoretically it is impossible to reach 100% efficiency, as the semiconductor materials or combination of them are suited only for specific spectral ranges. The energy of the rest of the spectrum cannot be utilized, because the light quanta (photons) in that range do not have enough energy to "activate" the charge carriers. A certain amount of this surplus photon energy is transformed into heat rather than into electrical energy. The maximum efficiency of the energy conversion can be determined by the help of

$$\eta = \frac{W_g \int_{W_g}^{\infty} N(W_p) dW_p}{\int_0^{\infty} W_p N(W_p) dW_p} \quad (1)$$

formula. Where $N(W)$ is the photon density function and W_g is the energy necessary to activate a charge carrier, in case of semiconductor materials W_g is equal to the band gap. If W_g is low many electron-hole pairs are generated, but their energy will be low, as well. However, if W_g is high, though the energy of the electrons will be high, the number of them will be little. Let's approximate the spectrum of the sun with a black body, which is at 5800K temperature. In this case the efficiency in the function of W_g , based on equation (1), has the following shape (Fig. 1).

It can be seen that the efficiency has its maximum, approximately 44%, around $W_g = 1.1\text{eV}$. This is not the efficiency of the solar cell, but the efficiency of the photon-electron conversion. In case of semiconductor solar cells the voltage at the terminals is limited by the forward voltage. The maximum efficiency achieved in case of monocrystalline silicon solar cells is 24% in laboratory, but it is not more than 14-17% in batch production. The efficiency of GaAs solar cells is better, but their manufacturing costs are higher, as well.

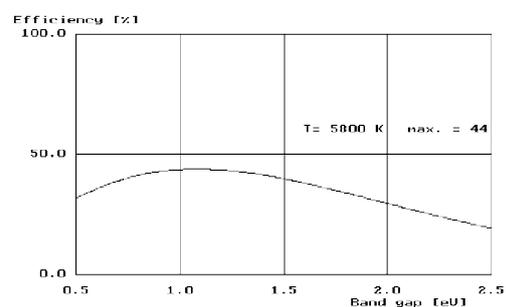


Fig. 1 The maximum efficiency of the energy conversion

The electrochemical solar cells are relatively simple solar cells. The photoelectric transformation of solar energy into electric energy or into storable chemical energy source (hydrogen) has three steps. The first step is excitation of electrons by photo absorption. This can be done either by means of semiconductors or by photosensitive electrochemical reaction. The second step is the separation of charge carrier pairs by electric field. Finally the energy in the electrons and holes is utilized by reduction or oxidation of the molecules in the electrolyte.

The electric field necessary for the charge separation does not only exist at solid state – semiconductor (having different potential barrier) interface, but also at electrolyte-semiconductor interface, too. The choice of electrolyte (to have appropriate redoxpotential) and semiconductor (to have appropriate forbidden gap) is important both for optimum utilization of solar energy and for development of high enough electric field at the interface. If the semiconductor is n type then due to the direction of the developed electric field the generated electrons are drifted towards inside the semiconductor, while the holes propagate towards the interface. In p-type semiconductor the direction of the developed electric field is opposite and so is the movement of the charge carriers. At the interface charge transport takes place into the redox system. Then, in case of n-type semiconductor the oxidized, in case of p-type material the reduced molecules diffuse away from the surface. The charge transport

takes place until the equilibrium state has been established. At this time potential difference can be measured between the semiconductor and the electrolyte. This potential difference can deliver power if it is connected into an electric circuit. The energy conversion works permanently if the redox system is regenerative, i.e. if the oxidized (reduced) system on the semiconductor is reduced (oxidized) back at the metal electrode.

2. THE ELECTROCHEMICAL SOLAR CELL

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. Direct energy conversion relies on the semiconductor material, which can absorb a fraction of the solar spectrum depending on its W_g bandgap energy. Unfortunately, many materials with adequate bandgaps are susceptible to photocorrosion, due to destructive hole-based reactions. Also, the semiconductors less susceptible to photocorrosion, such as metal oxides like TiO_2 and SnO_2 , exhibit a too large bandgap to permit significant collection of visible light.

An alternative to overcome the limited spectral sensitivity of the wide bandgap semiconductors, which are restricted to UV light, is surface modification with visible-light absorbing dye molecules. The sensitization of semiconductors using dyes is a century old, when it was used in the development of photography. Their application in solar energy conversion is more recent, and progressed considerably after the seventies, with the advanced in the development of dye sensitizers, especially bipyridyl Ru complexes with anchoring groups to attach them to the semiconductor surface.[2]

Ruthenium based dyes, and specially those casting pyridil ligands, have proven very effective in photovoltaic conversion. Their molecular properties, and the possibilities of related applications, are directly related to: (a) the energetic spectrum of the molecules that determines the optical absorption and emission characteristics; (b) the molecular electron density (and its polarizability) which is associated to the reactivity of the molecule.

Photoelectrochemical cells based on dye-sensitized semiconductor electrodes also include solutions containing a suitable redox couple and a counter-electrode. The illumination of the dye to an electronically excited state which is quenched by electrontransfer to the conduction band of the semiconductor, leaving the dye in an oxidized state.

The oxidized dye is reduced by the electron donor present in the electrolyte. The electrons in the conduction band are collected, flow through the external circuit to arrive at the counter-electrode, where they cause the reverse reaction of the redox mediator. Thus, the photoelectrochemical cell is also regenerative and the process leads to direct conversion of sunlight into electricity. If only the above reactions took place, the solar cell would be stable, delivering photocurrent indefinitely. The maximum photovoltage, at open circuit potential (V_{oc}), is the difference between the Fermi level of the semiconductor under illumination and the redox potential of the mediating redox couple. The photocurrent yield depends on the spectral and redox properties of the dye, its excited state lifetimes, the efficiency of charge injection, the ionic conductivity of the electrolyte to collect and channel the electrons through the external circuit.

The redox couple in the electrolyte also is crucial importance for stable operation of a dye-sensitized solar cell, because it must carry the charge between the photoelectrode and the counter-electrode for regeneration of the dye. After electron injection, the electron donor in the electrolyte must reduce the oxidized dye to the ground state as rapidly as possible. Thus, the choice of this charge mediator should take into account its redox potential, which must be suitable for regenerating the dye. Also, the redox couple must be fully reversible and should not exhibit significant absorption of visible light. Another important requirement is related to the solvent, which should permit the rapid diffusion of charge carriers, while not causing the desorption of the dye from the oxide surface.

The band diagram of the dye-sensitized photoelectrochemical solar cell is shown in Fig. 2.

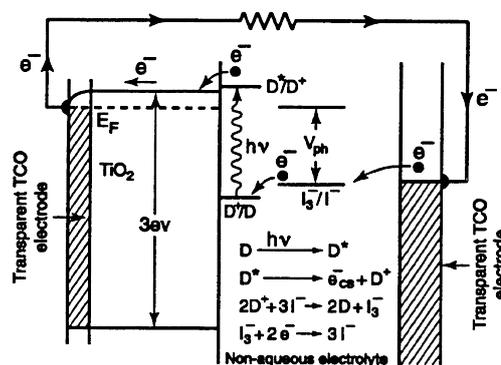


Fig. 2 The band diagram of the dye-sensitized photoelectrochemical solar cell

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 .

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 [3]. The band gap and type of band transition was determined by absorption and the I-V characteristics was determined by photoelectro-chemical method [4]. Furthermore it was found that this material shows very good resistivity against photocorrosion [5]. 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 [6].

3. 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 [7]. 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.

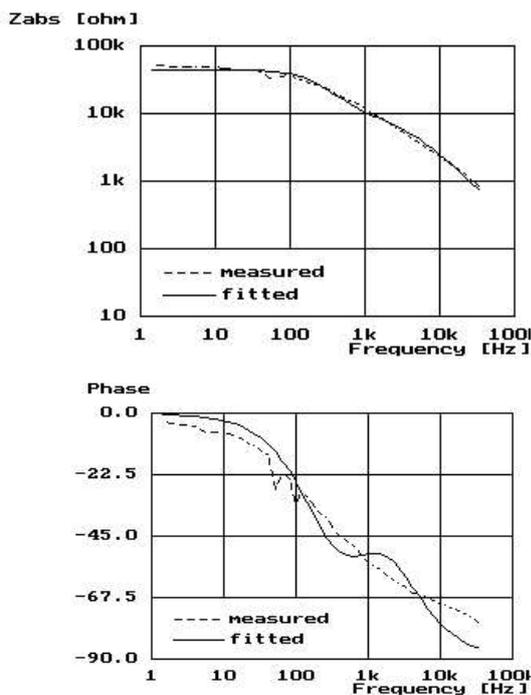


Fig. 3 The amplitude and phase diagrams of the Cd_4GeSe_6 and 0.05 M H_2SO_4

4. PHOTOELECTROCHEMICAL INVESTIGATION

The band gap was determined by absorption [4] and photoelectrochemical [8] methods and was found to be 1.7 and 1.75 eV respectively. A further reference [9] gives 1.5 eV band gap and indirect band transition. Ref. [10] gives 1.9 eV for band gap from photoluminescence measurement at 10 K. These strongly different photoelectrochemical and photoluminescence results are reviewed in Ref. [4].

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 [6]. 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 [11]. 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 $\text{k}\Omega/\text{mm}^2$. R_2 and C_2 represent the surface levels and deep centers where the values range between 0.6 and 1.6 $\text{k}\Omega/\text{mm}^2$ 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 than in H_2SO_4 solution. Measured and fitted amplitude and phase diagrams of the junction are shown in Fig. 3.

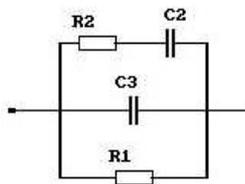


Fig. 4 The simple equivalent circuit

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 $\text{k}\Omega/\text{mm}^2$. The values of the elements of the RC circuit which represent the surface levels are 1.7 $\text{k}\Omega/\text{mm}^2$ 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 [5].

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BIOGRAPHY

Péter Turmezei was born in Budapest, Hungary in 1949. He received the electrical engineering degree from the Technical University of Budapest, Hungary in 1973, the dr. techn. degree in 1986 and the PhD degree in 2003. He joined the *Research Institute for Particle and Nuclear Physics of Central Research Institute for Physics* in 1973, where his job was designing and testing nuclear measuring equipments. Since 1975 he worked at the Research Institute for Telecommunication on the field of analogue and digital circuit design, development of equipments and systems for telecommunication. Since 1987 he has been Associate Professor at the Institute of Microelectronics and Technology of the Kandó Kálmán Polytechnics of Budapest. Currently he is the head of the Institute. His latest research interests include semiconductor technology and solar cells.