

THERMODYNAMIC MODELLING OF ELECTRONIC MATERIALS

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Received 1 June 1998, in revised form 30 November 1998

Abstract. The process of materials preparation is a typical physico-chemical process operated by classical physico-chemical parameters such as temperature, pressure, and the composition of materials. The review offers examples of how the thermodynamic modelling has been used for the characterization and preparation of two different types of electronic materials – semiconductive compounds and conductive polymers.

Key words: thermodynamic modelling, A_2B_6 semiconductive compounds, polyparaphenylene, polypyrrole, polyaniline.

INTRODUCTION

Industry needs materials and devices with well-defined physical and chemical properties produced by controllable technologies. The technically important parameters of the devices depend strongly on the properties of the initial material used, mainly on its defect structure. The situation is especially complicated in the preparation process of electronic materials where very small amounts of the materials structure elements – native defects or foreign atoms – have an extremely strong influence on the physical parameters of the device. Usually, the process of materials preparation can be described as a typical physico-chemical process operated by the classical physico-chemical parameters such as temperature (T), pressure (P), and material composition (X). The spectrum of the characteristic parameters of the final materials and devices is wide and may include electrical conductivity, magnetic properties, optical properties, microstructure of thin films, granulometry of powders, and the anticorrosion stability of the materials. Therefore, it is necessary to show the correlation between the

parameters describing the process and the parameters describing the final material with a view to develop effective technologies for obtaining electronic materials. The description of this process via the thermodynamic parameters correlated to the physical properties of the prepared base materials is called the thermodynamic modelling in this review. The thermodynamic modelling gives us a theoretical tool for correlating the parameters of different processes of materials preparation to the physical properties and chemical composition of the materials and/or devices produced. The principle of the thermodynamic modelling is presented schematically in Fig. 1.

Our task in using the thermodynamic modelling is to describe theoretically the investigated material as a thermodynamic system. It means that we must point out the defects responsible for the physical and chemical properties of the material and the relations between them. Usually, it is possible to characterize these defects as the structure elements of materials thermodynamically by additional spectroscopic, magnetic, optical, chemical, and other methods. On the other hand, we can measure certain physical parameters or chemical properties of the base materials and point out the defects responsible for the respective properties. Under the equilibrium conditions these defects are described by the laws of thermodynamics and operated by the thermodynamic parameters P , T , and X . Therefore, in order to predict the physical and chemical properties of materials it is necessary to describe their preparation process as a model where the characteristic physical or chemical parameters of the materials are presented as the functions of temperature, pressure, or composition, and to control this model by experiments. In the following parts of our review we would like to offer some illustrations of how the thermodynamic modelling has been used at Tallinn Technical University for the characterization and preparation of different materials – semiconductive compounds and conductive polymers.

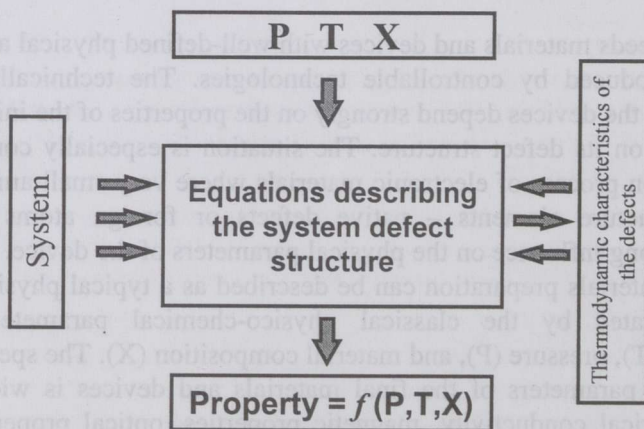


Fig. 1. Scheme of the thermodynamic modelling of electronic materials.

INVESTIGATIONS OF DEFECT STRUCTURE

For thermodynamic modelling of electronic materials exact description and investigation of the defect structure of the materials are essential. In practice the investigation of the defect structure gives correct data only under the conditions of thermodynamic equilibrium, usually at high temperatures. Some approximations allow us to transfer the high-temperature defect structure to lower temperature (usually room temperature) conditions.

High-temperature electrical conductivity

To apply thermodynamic modelling in the study of technological processes and/or materials, it is necessary to design an experimental set-up that allows us to modify the system or material by changing the thermodynamic parameters P , T , and X . On the other hand, it is necessary to identify the physical parameters that describe precisely the defect structure of the materials or the device properties. The dependence of these physical parameters on the thermodynamic ones, measured under the system modification conditions, gives us a possibility to characterize the structure and properties of the materials. This experimental set-up has also to allow modification of the system or material investigated without any direct physical measurements. Such a process is called doping. The principles of that kind of high-temperature experiments were described by Kröger [1] and were developed for A_2B_6 materials and conductive polymers by scientists at Tallinn Technical University [2, 3]. As a typical example of the system of modification and investigation the electrical conductivity of the electronic materials, primarily the A_2B_6 materials, is presented in Fig. 2.

The crystal and defect structures of the A_2B_6 semiconductive materials and conductive polymers are different, which leads to differences in the preparation technology of these groups of materials. For example, the usual doping method for the polymer materials is doping from the solutions or electrochemical doping [4]. At the same time the gas-phase high-temperature doping is generally used for A_2B_6 semiconductive materials [1]. Despite this fact our system, illustrated by Fig. 2, allows us to use high-temperature modelling also for the conductive polymers and to measure their electrical conductivity during the doping process. According to our experiments the use of this system leads to high-stability conductive polymers and additionally allows investigation into the kinetics of the doping process.

The typical result of the high-temperature conductivity investigations is the model of the defect structure of the electronic materials – the dependence of the structural defect concentrations on the temperature or component vapour pressure (deviation from the stoichiometry). The information obtained is very useful for the technologists working in the field of materials preparation. Usually it is enough to determine the dominating defects by the so-called Brouwer approximation method (Fig. 3) [1, 3, 5]. High-temperature investigations give us

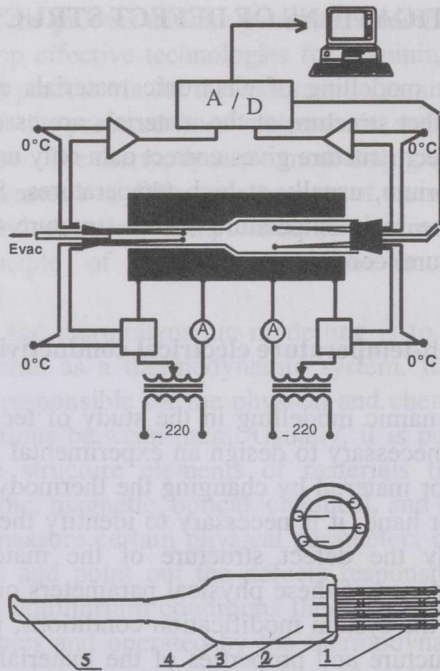


Fig. 2. The system and ampoule for the high-temperature doping and conductivity measurements. 1, quartz removals for the electrodes; 2, sample for modification or conductivity measurements; 3, tungsten electrodes; 4, quartz tube; 5, doping component reservoir [2].

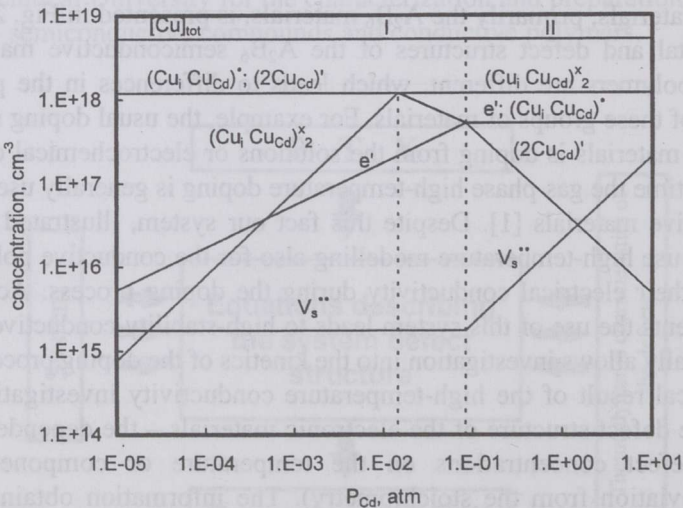


Fig. 3. Cd vapour pressure dependence of defect concentrations for CdS:Cu ($5 \times 10^{18} \text{ cm}^{-3}$) at $800 \text{ }^\circ\text{C}$ [3].

also information on the thermodynamic properties of these structure elements (enthalpies, entropies) and the kinetic and transport properties of materials (activation energies of the electrical conductivity, diffusion coefficients) [3, 5].

Electrical conductivity and kinetic investigations with the high-temperature technique applied showed that the conductivity mechanism of the doped polyparaphenylene is in agreement with the variable-range-hopping model and the polarons and bipolarons were determined to be the dominating defects [6–8].

Phase equilibrium and solubility of the components

The phase equilibrium investigations made applying the high-temperature experimental technique give additional information on phase transitions and structural defect equilibrium in different A_2B_6 semiconductive systems, especially in the multicomponent systems [9, 10].

The investigations of the solubility of the components in A_2B_6 semiconductive compounds in dependence on the vapour pressure of the components using the two-zone set-up (Fig. 2) give additional information on the possible phase equilibrium ranges of the investigated systems. The dependence of the solubility of doping components on the stoichiometry of the materials at different temperatures and vapour pressures of components allows us to connect the obtained results with the information on the defect structure from high-temperature conductivity measurements and with the phase diagrams of the investigated systems (Fig. 4) [9].

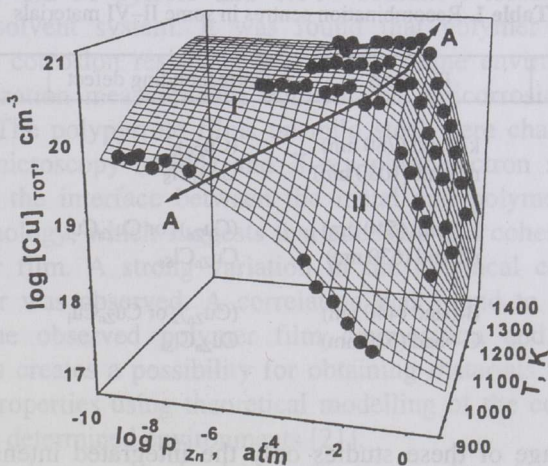


Fig. 4. Cu solubility in ZnS. The line A-A is the range boundary.

LOW-TEMPERATURE METHODS

The optoelectronic properties of semiconductive materials and devices are closely connected with the structure of the crystal lattice and particularly with the point defects structure of the material. An understanding of the chemical and physical nature of the point defects and their complexes in A_2B_6 compounds is very important for the control of both their electrical and optical properties. In the previous chapter we described the results of the investigations of the defects in semiconductive materials and conductive polymers at high temperatures, but the main problem is that in practice these materials and devices will be used at low temperatures, where the high-temperature defect structure changes drastically. To solve this problem, a new model was proposed by the Chair of Semiconductor Materials Technology. This model combines the low-temperature properties of the semiconductors (photoconductivity, luminescence) with high-temperature defects. At first, only the influence of the materials preparation conditions (concentration of impurities, partial vapour pressure of the components, thermal annealing temperature) on the integral intensity of the emission bands (PL-bands) in the luminescence spectra was used as the source of information [11, 12]. The integral intensity dependencies were used to clarify the chemical nature of the recombination centres (Table 1) and also the enthalpies of the cluster formation of the quasichemical reactions. Thus, it became possible to determine the chemical nature of radiative and non-radiative recombination centres and also the chemical nature of the predominant impurities and charged defects at low temperatures. As a result the defect structures of $CdS:Cu:Cl$, $ZnSe:Cu:Cl$, $ZnS:Cu:Cl$, $CdS:Ag:Cl$, and $CuInSe_2$ were established [11, 13–16].

Table 1. Recombination centres in some II–VI materials

Material	PL-band	Corresponding defect	Reference
$CdS:Cu:Cl$	k-Band (780 nm) r-Band (1030 nm)	$(Cu_{Cu})_2$ $Cu_{Cd}Cl_S$	[15]
$ZnSe:Cu:Cl$	k-Band (540 nm) r-Band (630 nm)	$(Cu_{Zn})_2$ or $Cu_{Zn}Cu_i$ $Cu_{Zn}Cl_{Se}$	[13]
$ZnS:Cu:Cl$	B-band (440 nm) G-band (520 nm)	$(Cu_{Zn})_2$ or $Cu_{Zn}Cu_i$ $Cu_{Zn}Cl_S$	[16]

In an early stage of these studies only the integrated intensity of different luminescence bands was used as a physical parameter, although the luminescence spectrum contains much more information. Later the method was elaborated and a new, more physical approach was developed. The new approach

is based on the effect of the so-called physical structure of recombination centres on the optoelectronic properties of wide bandgap semiconductors. As a result of these studies it became obvious that most of the important recombination centres and also the dominating impurity defects in A_2B_6 materials are complexes with two or more point defects [11, 17–19]. In addition, the impact of the surrounding lattice on the recombination parameters of centres was further clarified.

PRACTICAL APPLICATIONS OF THE INVESTIGATED MATERIALS

The high- and low-temperature investigations yield theoretical values of the thermodynamic properties of the investigated system, such as the enthalpies of the defects formation, ionization energies, etc., which could be used for the material defect structure calculations. In addition, the thermodynamic modelling of electronic materials gives useful technological recommendations, which have been used in various new and promising practical applications.

Conductive polymers

The interest in the application of electrically conductive polymers as anti-corrosion materials has increased remarkably in recent years. Electrochemical synthesis of polypyrrole was performed from aqueous solution directly onto a stainless steel electrode with the aim of testing the possibility of using polypyrrole as an anticorrosion coating. Polypyrrole thin films were deposited galvanostatically (2 mA/cm^2) on steel electrodes at the temperature of -5°C from the solution of 0.2 M pyrrole and 0.1 M sodium *p*-toluensulphonate in an ethanol/water solvent system. It was found that polymer coating increases remarkably the corrosion resistance of steel in saline environments. Potentiodynamic polarization measurements confirm the anticorrosion effect of these coatings [20]. The polypyrrole films on mild steel were characterized through atomic force microscopy (AFM) and X-ray photoelectron spectroscopy. The AFM study of the interface between the metal and polymer shows areas of different morphology, which suggests that adhesive and cohesive failures occur in the polymer film. A strong variation in the chemical composition at the interfacial layer was observed. A correlation was found to exist between the variation of the observed polymer film composition and its anticorrosion properties. This creates a possibility for obtaining materials with the predicted anticorrosion properties using theoretical modelling of the conductive polymer coatings for the determined environments [21].

Conductive polymers can also be an effective medium for chemical sensing, based on the electronic changes occurring in the polymeric films with the gas-phase adsorption of electronically active vapours.

The dependence of the quartz crystal microbalance (QCM) polyaniline and polypyrrole sensors on the relative humidity of air has linear character in the whole investigated range of relative humidity. The parameters of the obtained polyaniline and polypyrrole QCM humidity sensors (relatively high speed, wide working range, simple electronic control) allow their use in industry, in domestic conditions, and in environmental protection [22].

A_2B_6 semiconductive materials

CdTe is an A_2B_6 semiconductor with an ideal 1.45 eV bandgap for direct light-to-electricity conversion. The recent progress in the development of CdTe based thin film solar cells has increased the interest in the polycrystalline form of CdTe as this material can be used as a starting material in the processes of low-cost production of thin films. In recent years several investigations on radiative electron-hole recombinations in CdTe single crystals have been performed and published [23]. However, there is a lack of experimental information on the radiative recombination centres in the powder samples of CdTe. Latest research has shown an increasing importance of understanding the behaviour of the defects in CdTe. It has been understood that improving the CdTe based solar cell parameters without precise information about the defect structure of materials is impossible. In the CdTe based solar cell it is important to reach and maintain a high level of p-type conductivity and therefore the stability of defects is also very important. Despite the numerous recent studies in this field, the defect structure and the physical processes giving rise to high p-type conductivity in CdTe are still subject to discussion.

Although the majority of defects in CdTe are radiative recombination centres and may be detected by photoluminescence studies, there are some defects that act as nonradiative centres and therefore these could be detected only by electrical measurements. The combination of photoluminescence measurements with electrical measurements in order to get a more definite description of the defect structure [24] has led to new and promising results. A new model, which associates conductivity, photoconductivity, and photoluminescence in CdTe:Cl, was proposed. At low Cl concentrations the complexes Te_iCl_{Te} and $V_{Cd}Cl_{Te}$ are responsible for low p-type resistivity in CdTe. At higher chlorine concentrations the Te_i2Cl_{Te} and $V_{Cd}2Cl_{Te}$ formed increase the p-type resistivity. New PL-bands were found in the CdTe whose intensity is in good correlation with the p-type electroconductivity in CdTe. High concentrations of chlorine lead to the formation of defect Cl_{Te} , causing high resistivity and photoconductivity in CdTe. These results gave a basis for the development of a new technology based on the vacuum annealing method, which remarkably improves the p-type conductivity of CdTe [25]. As a result materials with high p-type conductivity were developed.

CONCLUSIONS

The thermodynamic modelling is a powerful tool in studying solid state materials and producing materials with predicted properties. The modelling is universal and applicable to a wide range of electronic materials: from traditional semiconducting compounds to a new class of electronic materials – conductive polymers.

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ELEKTRONMATERJALIDE TERMODÜNAAMILINE MODELLEERIMINE

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Elektronmaterjalide ja nendel põhinevate seadiste ning tehnoloogiliste rakenduste saamine on tüüpiline füüsikalise-keemiline protsess, mida juhitakse oleku parameetritega, nagu temperatuur, rõhk ja koostis. Seadiste ja tehnoloogiliste rakenduste omadused omakorda määratakse materjalide defektstruktuuriga. Defektstruktuur on määratud materjalide valmistamise tehnoloogilise protsessi parameetritega, mis sageli langevad kokku oleku parameetritega. Etteantud omadustega seadiste ja materjalide saamiseks on vaja tunda seoseid materjalide struktuuri ning füüsikaliste ja keemiliste omaduste vahel. Käesolevas töös on kokku võetud hulk näiteid, kus etteantud omadustega A_2B_6 -tüüpi pooljuhtmaterjalide ja juhtivate polümeeride valmistamise protsessi on analüüsitud tervikliku protsessina termodünaamika seaduspärasusi silmas pidades.