

# Transparent Conducting Oxides: Selected Materials for Thin Film Solar Cells

E. Lara-Padilla<sup>1</sup>, Maximino Avendaño-Alejo<sup>2</sup>, L. Castañeda<sup>3</sup>

<sup>1</sup>Sección de Estudios de Posgrado e Investigación de la Escuela Superior de Medicina, Instituto Politécnico Nacional, Plan de San Luis y; Díaz Mirón S/N, Casco de Santo Tomás, Alcaldía Miguel Hidalgo, C. P.11340, Cd. de México, México

<sup>2</sup>Instituto de Ciencias Aplicadas y Tecnología, Universidad Nacional Autónoma de México, C. P.04510, Apdo. Postal 70-186, CDMX., Mexico

<sup>3</sup>Universidad Estatal del Valle de Ecatepec, Av. Central s/n, Valle de Anáhuac, 55210. Ecatepec de Morelos, Estado de México, México. E-mail address: [otilioh\[at\]yahoo.com.mx](mailto:otilioh[at]yahoo.com.mx); Tel: + (52) 55 8021 1981

**Abstract:** *Current photovoltaic technologies, as well as next-generation approaches to PVs, will place specific demands on the transparent contact layers beyond transparency and low resistivity. The mainstay of the transparent conducting oxides used today is based on indium tin oxide because, at present, no other TCO delivers the same performance and versatility. The high cost of In as a raw material and process restraints, however, make this oxide system less attractive for low-cost, high-volume PV applications. Alternative TCO materials, such as ZnO, appear to be promising for some of these applications, but processing and performance issues remain. In many of the novel PV technologies currently under development, such as organic photovoltaics, control of the morphology and surface chemistry of the TCOs used is critical to device performance. Examination of current and future PV-TCO materials performance leads to the conclusion that new efforts to develop application-specific TCO materials and processes are needed. As new device structures evolve, it will be necessary to expand the toolkit of TCO materials available to take advantage of very different film properties and surface chemistries.*

**Keywords:** industry and finance integration, industry and finance integration, informatization

## 1. Introduction

During these last years, many improvements on the performances of the photovoltaic cells have allowed to obtain high conversion efficiency at low cost. One of the key factors to obtain photovoltaic structures of high-efficiency energy conversion are the transparent conducting oxides, which play a significant role in the manufacture of this type of cells. For this reason, there has been a renewed interest in many R&D laboratories all around the world on the study of the transparent conducting oxides.

Thin films of these materials are produced by several deposition techniques, e. g. evaporation, sputtering, chemical vapour deposition, spray pyrolysis, etc. The most studied transparent conducting oxides are: SnO<sub>2</sub>: F (FTO), ZnO: Al (AZO), In<sub>2</sub>O<sub>3</sub>: Sn (ITO), and Cd<sub>2</sub>SnO<sub>4</sub> (CTO) [1]. These metallic oxides exhibit very good optical transparency nearly or more than 90% for visible light and near infrared radiation and very high *n*-type conductivity. For these reasons transparent conducting oxides are generally nearly degenerate semiconducting materials with a free carrier concentration between 10<sup>18</sup> cm<sup>-3</sup> and 10<sup>20</sup> cm<sup>-3</sup>. The high transparency and also the high electrical conductivity make the transparent conducting oxides suitable for a great variety of applications. In fact they are used in optoelectronic devices and as transparent electrode in photovoltaic modules.

Since it is not possible to obtain both high electrical conductivity and optical transparency in any intrinsic material, one way to reach this aim is to create electron degeneracy in a wide band-gap oxide. This could be made in two different ways:

- Introducing donor elements into the oxide matrix.
- Exploiting deviation from correct stoichiometry by, for example, using structural defects and/or oxygen vacancies.

The first point is explained by considering the substitution of a higher valence cation by a donor impurity in the oxide, e. g. tin or antimony in indium oxide or fluorine in tin oxide, increases the electron concentration and so the *n*-type conductivity. On the contrary, the replacement of a lower valence cation by an acceptor impurity generates a hole (broken bond) that works like a trap (deep level in the energy gap) in the *n*-type metallic oxide decreasing its *n*-type conductivity.

Since the mean grain size of transparent conducting oxide thin films is in the range of 10–100 nm depending on the deposition method, the high electrical conductivity of doped and undoped films depends mainly on carriers (electrons) concentration and not on their mobility. This is due to the fact that the mobility in these films is considerably lower than that in the bulk materials, because it is limited by grain boundaries.

In the last few years a lot of new transparent conducting oxides have been developed starting from multicomponent oxides such as: GaInO<sub>3</sub>, ZnSnO<sub>3</sub>, Cd<sub>2</sub>Sb<sub>2</sub>O<sub>6</sub>: Y, Zn<sub>2</sub>SnO<sub>4</sub>, MgIn<sub>2</sub>O<sub>4</sub>, In<sub>4</sub>SnO<sub>12</sub> [2]. All these metallic oxides can exhibit high *n*-type conductivity following the behavior described above.

In addition, a new  $p$ -type transparent conducting oxides has been intensively studied in recent years in order to make a  $p$ - $n$  junction. In 1997 it was reported for the first time that a  $\text{CuAlO}_2$  thin film exhibits  $p$ -type conductivity.

After that, a new series of materials based on copper was discovered such as:  $\text{CuGaO}_2$  and  $\text{SrCu}_2\text{O}_2$  [3, 4]. In 2000, a UV-emitting diode based on a  $p$ - $n$  heterojunction composed of  $p$ - $\text{SrCu}_2\text{O}_2$  and  $n$ - $\text{ZnO}$  was successfully fabricated using heteroepitaxial thin film growth.

Anyway, the major area of interest is in  $n$ -type transparent conducting oxides due to their utilization in industrial applications. One of these applications is in photovoltaic (PV) module fabrication. In this case, it is necessary to reach a very low resistivity. This direction has been strongly accelerated by the rising demand for enlargement of the module size.

In PV module production the specification needed for transparent conducting oxides not only concerns the very high electrical conductivity and very high optical transparency but also their chemical and physical stability [5].

In this Chapter we will try to give an overview of the present uses of transparent conducting oxides in PV R&D.

## References

- [1] K. L. Chopra, S. Major, D. K. Pandya, *Thin Solid Films* 102, 1–4 (1983).
- [2] T. Minami, Y. Takeda, S. Takata, T. Kakumu, *Thin Solid Films* 308–309, 13–18 (1997).
- [3] K. Ueda, T. Hase, H. Yanagi, H. Kawazoe, H. Hosono, H. Ohta, M. Orita, M. Hirano, *J. Appl. Phys.* 89, 1790–1793 (2001).
- [4] A. Kudo, H. Hanagi, H. Hosono, H. Kawazoe, *Appl. Phys. Lett.* 73, 220 (1998).
- [5] N. Romeo, A. Bosio, V. Canevari, M. Terheggen, L. Vaillant-Roca, *Thin Solid Films* 431–432, 364–368 (2003).

## 2. Transparent Conducting Oxides Evaluation

### 2.1. First Approach: Electrical and Optical Properties

Transparent and conducting oxide thin films have figured prominently for many years in a wide variety of applications, such as heating elements on aircraft windows for deicing and defogging, antistatic coatings on instrument panels, and electrical contacts in liquid crystal electrochromic and electroluminescent displays. The high reflection in the infrared region, in conjunction with high transparency in the visible region, has been exploited to make heat reflecting mirrors. These films have also become an important part on the development and present uses of thin films photovoltaics.

The basic desired properties of a transparent conducting film are a high bandgap, above about 3.0 eV, and a low effective mass and high carrier mobility. The most common used transparent conducting oxide films have been those of  $\text{SnO}_2$ ,  $\text{In}_2\text{O}_3$  and  $\text{Cd}_2\text{SnO}_4$ . Recently,  $\text{ZnO}$  films possessing good

transparent electrode properties have been prepared. To compare the performance of different oxides, Fraser and Cook [1] have defined a quantity, called figure of merit,  $F_{\text{TC}}$ , expressed as  $F_{\text{TC}} = T/R_{\text{sh}}$ , which relates the optical transmission and sheet resistance. This definition weighs too much in favour of the sheet resistance. A modified definition, more appropriate for solar cells, has been given after by Haacke [2] and is expressed as:

$$\phi_{\text{TC}} = T^{10}/R_{\text{sh}} = \sigma t \exp(-\alpha t) \quad (1)$$

Where  $T$  is the transmittance,  $R_{\text{sh}}$  is the sheet resistance,  $\sigma$  is the conductivity,  $\alpha$  is the absorption coefficient, and  $t$  is the thickness of the coating. For a given sheet resistance, the figure of merit  $\phi_{\text{TC}}$  can be related to basic material parameters by the expression

$$\phi_{\text{TC}} \sim \exp(-\text{constant} \cdot \alpha/\sigma) \quad (2)$$

A maximum value for  $\phi_{\text{TC}}$  can be obtained only when  $\alpha/\sigma$  is a minimum.  $\alpha/\sigma$  is given by

$$\alpha/\sigma = e/(\pi c n \nu^2 \mu^* m^*) \quad (3)$$

where  $\mu = e\tau/m^*$  is the mobility of free electrons in the conduction band,  $m^*$  is the effective mass of free carriers,  $\tau$  is the relaxation time,  $n$  is the refractive index,  $e$  is the electronic charge, and  $c$  is the velocity of light. It is those clear that  $\alpha/\sigma$  will be a minimum when  $\mu$  is high and  $m^*$  is low, since  $\mu$  is related to  $m^*$  by

$$\mu = (m^*)^{-x} \quad (4)$$

where  $x \sim 1.35$  for many semiconductor materials [3].

From eq. (3) it becomes that a good transparent conducting oxide must be characterized by a low effective mass and high carrier mobility. The low the effective mass and the high the carrier mobility is, the higher the figure of merit will be (more transparent and less resistive the material, according to eq. 1).

There have been also alternative definitions for the figure of merit [4], but the one given by Haacke remains the only widely used today, owing to its precise and simple way it uses to relate the basic material properties.

A variety of techniques have been employed to deposit transparent conducting oxides. These include dc [1, 5-10], rf [11-16] and ion beam [8, 17] sputtering, ion plating [18], spray pyrolysis [19-26], chemical vapor deposition (CVD) [27, 28], electron beam [29], flash [30], reactive [31-33], and activated reactive [34] evaporation, and anodization [8].

### 2.2 Going a Step Further: Chemical and Physical Stability Concerns

Each PV technology has different requirements for the transparent conducting oxide layer, leading to a reexamination of these materials. Coupled to this is an effort to make conventional cells more efficient by improving the junction characteristics.

Many of the new PV technologies extent well beyond the conventional transparent conducting oxide characteristics of transparency and conductivity. There is, for instance, an increasing desire to employ transparent conducting oxide layers as diffusion barriers (like i-ZnO/Al: ZnO in Copper-Indium-Gallium-Selenide-CIGS-cells), to control the contact work function (like in Organic Photovoltaics-OPV -), to provide an interface with organic and other materials (like in Grätzel-Dye-sensitized TiO<sub>2</sub>-cell), and to have the transparent conducting oxide also act as a light trap (like ITO in Heterojunction with Intrinsic Thin layer-HIT-cell).

Low process temperatures and increased process flexibility are critical for many devices. Very low cost techniques such as sol-gel spin-coating [35, 36], doctor balding [37, 38], spray coating (not to confound with spray pyrolysis, that is a kind of vapor phase temperature-driven process) [39], reel-to-reel slot-die coating [40] and printing techniques (inkjet, flexography and gravure printing) [41] have gained interest, owing to its flexibility and high productivity (high production rates at very low production costs). This need for improved performance in a wide range of areas coupled with the ever-rising price of In is driving a renaissance in the investigation of novel transparent conducting oxides for PV application.

The various physical and chemical properties of interest and present uses for thin film solar cell applications are discussed briefly in the following sections.

## References

- [1] D. B. Fraser and H. D. Cook, *J. Electrochem. Soc.*, 119 (1972) 1368.
- [2] G. Haacke, *J. Appl. Phys.*, 47 (1976) 4086.
- [3] R. W. Keyes, *J. Appl. Phys.*, 30 (1959) 454.
- [4] V. K. Jain, A. P. Kulshreshtha, *Sol. Energy Mater.*, 4 (1981) 151.
- [5] W. R. Sinclair, F. G. Peters, D. W. Stillinger and S. E. Koonee, *J. Electrochem. Soc.*, 112 (1965) 1096.
- [6] E. Leja, T. Pisarkiewicz and A. Kolodziej, *Thin Solid Films*, 67 (1980) 45.
- [7] M. Hecq and E. Porteir, *Thin Solid Films*, 9 (1972) 341.
- [8] E. Giani and R. Kelly, *J. Electrochem. Soc.*, 121 (1974) 394.
- [9] J. A. Thornton and V. L. Hedgcoth, *J. Vac. Sci. Technol.*, 13 (1976) 117.
- [10] N. Miyata, K. Miyaka and S. Nao, *Thin Solid Films*, 58 (1979) 385.
- [11] G. Haacke, W. E. Mealmaker and L. A. Siegel, *Thin Solid Films*, 55 (1978) 67.
- [12] J. L. Vossen, *RCA Review*, 33 (1971) 289.
- [13] N. Miyata, K. Miyaka, K. Koga and T. Fukushima, *J. Electrochem. Soc.*, 127 (1980) 918.
- [14] H. W. Lehmann and R. Widmer, *Thin Solid Films*, 27 (1975) 359.
- [15] W. G. Haines and R. H. Bube, *J. Appl. Phys.*, 49 (1978) 304.
- [16] J. L. Vossen, in: *Physics of Thin Films* (Eds., G. Hass, M. H. Francombe, and R. W. Hoffman), Vol.9, Academic Press, New York (1976), p.1.
- [17] J. C. C. Fan, *Appl. Phys. Lett.*, 34 (1979) 515.
- [18] R. P. Howson, J. N. Avaratsiotis, M. I. Ridge and C. A. Bishop, *Appl. Phys. Lett.*, 35 (1979) 161.
- [19] J. Aranovich, A. Ortiz and R. H. Bube, *J. Vac. Sci. Technol.*, 16 (1979) 994.
- [20] E. Shanthi, A. Banerjee, V. Dutta and K. L. Chopra, *J. Appl. Phys.*, 53 (1982) 1615.
- [21] E. Shanthi, A. Banerjee and K. L. Chopra, *Thin Solid Films*, 88 (1982) 93.
- [22] E. Shanthi, V. Dutta, A. Banerjee and K. L. Chopra, *J. Appl. Phys.*, 51 (1980) 6243.
- [23] J. C. Manificier, L. Szepessy, J. F. Bresse. M. Perotin and R. Staek, *Mat. Res. Bull.*, 14 (1979) 109.
- [24] E. Shanthi, *Ph. D. Thesis*, Indian Institute of Technology, Delhi (1981).
- [25] H. Kostlin, R. Jost and W. Lerne, *phys. stat. sol. (a)*, 29 (1975) 87.
- [26] R. Groth, *phys. stat. sol.*, 14 (1966) 69.
- [27] B. J. Baliga and S. K. Gandhi, *J. Electrochem. Soc.*, 123 (1976) 941.
- [28] Y. S. Hsu and S. K. Gandhi, *J. Electrochem. Soc.*, 126 (1979) 1434.
- [29] A. K. Ghosh, C. Fishman and T. Feng, *J. Appl. Phys.*, 49 (1978) 3490.
- [30] J. C. Manificier, M. De Murcia, J. P. Fillard and E. Vicario, *Thin Solid Films*, 41 (1977) 127.
- [31] M. Mizuhashi, *Thin Solid Films*, 70 (1980) 91.
- [32] H. Watanabe, *Jpn. J. Appl. Phys.*, 9 (1970) 1551.
- [33] F. Van der Maesen and C. H. M. Witmer, *Proc. 7th Int. Conf. on Physics of Semiconductors*, Paris (1964), Academic Press Inc., New York, P.1211.
- [34] P. Nath and R. F. Bunshah, *Thin Solid Films*, 69 (1980) 63.
- [35] G. Yu, A. J. Heeger, *J. Appl. Phys.* 78 (1995) 4510.
- [36] J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* 376 (1995) 498.
- [37] C. J. Brabec, F. Padinger, J. C. Hummelen, R. A. J. Janssen, N. S. Sariciftci, *Synth. Met.* 102 (1999) 861.
- [38] F. Padinger, C. J. Brabec, T. Fromherz, J. C. Hummelen, N. S. Sariciftci, *Optoelectron. Rev.* 8 (4) (2000) 280.
- [39] D. Vak, S. Kim, J. Jo, S. Oh, S. Na, J. Kim, D. Kim, *Appl. Phys. Lett.* 91 (2007) 081102.
- [40] K. Schultheis, L. Blankenburg, S. Sensfuss, M. Schrödner, *Proceedings of the Cintelliq conference*, Frankfurt 2007.
- [41] Christoph J. Brabec and James R. Durrant, *MRS Bull.* 33 (2008) 670.

## 3. Transparent Conducting Oxides: Physics Related to Performance

Photovoltaic devices require at least one electrode that can provide optical access and low-resistance electrical connection at the same time. There are three classes of materials that meet well this properties: very thin pure metals, highly doped conjugated organic polymers and degenerated doped wide-bandgap oxide or nitride semiconductors. Other properties of interest, such as work function, band alignment, materials compatibility, processing and cost are also to be considered for photovoltaic applications.

From our discussion at section 2.1., it becomes obvious the need for high electrical conductivities to achieve low resistances, unless  $t$  is made unreasonably big. A simple analysis shows that electrical conductivities larger than  $10^3 \text{ ohm}^{-1}\text{cm}^{-1}$  are required for a good transparent conductor, and in the last years, in view of a growing demand for transparent conductors with even higher performance, the needs for conductivities approaching  $10^4 \text{ ohm}^{-1}\text{cm}^{-1}$  have become essential. Those values are, of course easily obtained from bulk pure metals. Unfortunately, in order to be transparent enough for practical applications (transmittances at least of 80%), they must be extremely thin. And when thinned to very small values, agglomeration and segregation effects appear on pure metals that renders them unusable for establishing a continuous film. Highly doped conjugated organic polymers are transparent enough, but their conductivities are still to be improved. From these last considerations, the choice is thus focused on transparent conducting oxides. These materials can be grown at reasonable thicknesses to avoid agglomeration and segregation problems, with conductivities near to  $10^4 \text{ ohm}^{-1}\text{cm}^{-1}$  and being still highly transparent in the visible range.

### 3.1. Structural Aspects

As a first instance, it becomes obvious that all physical properties of solid materials are related to its fundamental band structure, and from this, to its periodic distribution of potential. Crystal structure would appear then as a concern when we are interested on the optical and electrical performance of solids. From a physical basis, one could be tempted to consider amorphous materials as not well suited for uses as good transparent conductors, due to its very short-range order of the crystalline structure. However, this is not the case for all the metal oxides; indium oxide could yield usable transparent conducting properties even being amorphous.

There are several structural aspects that affect the properties of any thin film. We must cite stoichiometry, grain size, surface states, grain boundaries and grain growth orientation, energy band profiles, impurities, dislocations and interface states. Most of them are inter-related. Also, related to the interface states, it must be considered the structural affinity between the transparent conducting material and its neighbor layers as it can influence the performance of the device.

#### 3.1.1. Stoichiometry

As a general rule thin films are more susceptible to variations in stoichiometry than bulk materials both during and after formation. Effects at the surface such as chemical reaction, oxidation or the presence of surface states may affect a substantial proportion of the active region of a thin-film cell. Deposition and postdeposition environment must accordingly be closely controlled. In many cases stoichiometry controls the resistivity of the component materials. As a first-order effect stoichiometry may determine carrier density. The factors determining stoichiometry are dependent upon the means of preparation of the film, i. e., substrate and source temperatures for the process of arrival of the species, sticking coefficients, arrival rates upon the substrate and nucleation sites.

#### 3.1.2. Grain Size

The dominant structural difference between thick single crystals and most thin-film materials is the presence of grain boundaries. These have an electronic effect, because they represent a generally potent source of recombination. In the extreme, the ability of a cell to generate measurable short-circuit current can simply disappear. Under less extreme circumstances the effect of grain boundaries will be determined by the grain size, more specifically the ratio of grain size to film thickness, and the grain boundary recombination velocity. As it must be straightforward, grain size effects are minimized by achieving large  $r/t$  ratios, where  $r$  is the mean grain radius and  $t$ , as already mentioned, is the thickness of the film.

#### 3.1.3. Surface States

Surface states are of primary concern because of the presence of surface states and the associated effects on the device behavior. Based on the nature of the surface states, the energy bands can be bent so that minority carriers are either repelled or attracted to the surface. In the event that minority carriers are attracted to the surface, recombination is promoted, substantially reducing the short-circuit current obtainable from the cell. The effect on the short-circuit current of the effective surface recombination rate is a sharp reduction with an increase of surface recombination velocity and reduction in grain size. As for any component of a solar cell, in order to have good conversion efficiency, the effective surface recombination velocity must be small. This is generally described as a surface passivation which can be achieved in two fundamentally different ways. An appropriate doping profile will repel minority carriers from the surface, preventing surface recombination. Alternatively, a second layer can be created on the active absorbing material so that the surface states are neutralized, preventing them from acting as recombination centers. This last one is the most common form of use of transparent conducting layers for passivation effects.

#### 3.1.4. Grain Boundaries and Grain Growth Orientation

Recombination at grain boundaries are a potential source of serious carrier losses with corresponding reductions in short-circuit current. Junction area effects related to grain boundaries may also reduce the achievable open-circuit voltage. Grain boundaries may also result in enhanced diffusion of dopants. During a conventional diffusion anneal enhanced dopant penetration occurs down the grain boundaries. In extreme cases penetration right through the base layer can completely short out the device. Under less severe conditions a non-planar junction results. The grain boundaries can, in some cases, act beneficially by gettering impurities from the bulk, and it has been reported that appropriate doping results in band bending so as to eliminate recombination at the boundaries [1].

Grain boundaries may also affect the transport of majority carriers. Scattering effects or the existence of energy barriers can determine the effective carrier mobility and the resistivity of polycrystalline layers [2]. Macroscopic effects will then be apparent in increased series resistance and lower fill factors. Isolated grains smaller than the grid spacing will cause loss in the short-circuit current.

A simply cylindrical grain model can be used to discuss the types of problems that can occur in polycrystalline materials. The cylindrical grain is admittedly a major simplification but is probably adequate for treating films showing columnar growth. Other configurations of grain boundaries occur and may cause more severe problems. For example, a grain boundary parallel to the junction plane may restrict useful current generation to the region between the grain boundary and the junction.

### 3.1.5. Energy Band Profiles

Derived from their internal structure and effects related to the influence of the neighbor layers, varying energy levels can be formed in polycrystalline materials. This is generally referred to as band bending which acts in all respects like an internal electric field. Such a field can produce several effects, such as the surface passivation already discussed and modifications on the mobility of charge carriers. In this last case, in highly doped materials the mobility will be controlled by either neutral or charge-impurity scattering, resulting in reduced mobility and shorter diffusion lengths. Further effects are observed at very high doping densities. Lifetimes may be reduced by Auger mechanisms [3], and shrinkage of the band gap [4] may cause detectable losses in open-circuit voltage.

### 3.1.6. Impurities

We will distinguish between impurities and the intentional dopants which give *n*-or *p*-type character to the materials. Impurities will generally have a negative effect on the cell performance and may derive from the starting materials or become incorporated during cell fabrication. A range of deleterious effects can be traced to impurities such as deep levels which reduce carrier lifetime and diffusion length. Impurities may also lower mobility or create traps and charge centers which can affect the current-voltage behavior of the cell.

### 3.1.7. Dislocations

Dislocations can act directly as trapping and recombination centers or, by attracting impurities, become preferred sites for recombination, etc. In either case carrier lifetime and mobility may be adversely affected, and dislocation populations must be limited to achieve high conversion efficiency. Specific dislocation structures can be expected in most heterojunctions with significant effects on the interface recombination kinetics.

### 3.1.8. Interface States

The population of interface states in heterojunctions can be expected to depend on the formation technique, the component materials and the crystallography of the junction. Even in ideal cases, the mismatch in lattice constants will give rise to misfit dislocations with associated dangling bonds and interface states. Interface states have been shown to control all three major cell parameters in heterojunctions, short-circuit current, fill factor, and open-circuit voltage. Hence, control of interface state behavior is the key to producing successful thin-film solar cells from dissimilar materials.

The misfit dislocation array at the interface depends not only upon the lattice mismatch but also upon the thickness of the

layers. The initial layers of atoms deposited or grown on a bulk substrate will be strained to match the lattice constant of the substrate, but at a critical thickness, which depends upon the lattice mismatch and elastic constants of the materials, it becomes energetically favorable for misfit dislocations to form [5].

## References

- [1] H. J. Hovel, "Semiconductors and Semimetals", Vol.11, *Solar Cells*, Academic Press, New York, 1975.
- [2] L. L. Kazmerski, W. B. Berry, C. W. Allen, *J. Appl. Phys.*, 43 (1972) 3516, 3521.
- [3] D. Redfield, *Appl. Phys. Lett.*, 33 (1978) 531.
- [4] F. A. Lindholm, C. T. Sah, *IEEE Trans. Electron. Devices*, ED-24 (1977) 299.
- [5] C. A. B. Ball, C. Laird, *Thin Solid Films*, 41 (1977) 9.

## 3.2. Optical Properties

The optical properties of thin films should not differ significantly from those of the bulk single crystal. The optical band gap should be virtually the same except for strain effects. Absorption coefficients are an intrinsic property of the material and should not be significantly affected by going to thin films. The experimental measurement of the optical constants of thin films is beset with difficulties and considerable care must be taken to generate reliable results. Problems arise because of internal boundaries, mainly grain boundaries, which scatter and diffuse the light. In a traditional transmission experiment with normal incidence, scattering within the film may be measured as an apparent absorption. This spurious absorption effect due to scattering of the light out of the primary beam can be minimized but not eliminated by using a  $4\pi$  integrating reflectance sphere. Scattering at grain boundaries can result in some light approaching the exit surface at an angle larger than the critical angle for internal reflection. As a result, light is trapped within the film, giving an apparent absorption above that for a single-crystal film of the same thickness.

The surface region represents a large fraction of the volume of a thin film, and extra absorption at wavelengths longer than the bulk band gap can occur as a result of band bending. This effect can arise in both single and polycrystalline films. Band bending or gap shrinkage can also occur near grain boundaries, creating a further mechanism for enhanced absorption in a polycrystalline film.

For a transparent conducting oxide to be of interest for PV electrode applications, it must transmit freely across the solar spectrum. This defines the transmission window of this material as the range between both ends of the UV and the IR where the light must pass through the film. The short-wavelength (UV) cutoff corresponds to the fundamental band gap of the material, whereas the long-wavelength (IR) edge corresponds to the free carrier plasma resonance frequency. These critical optical properties are directly influenced by the carrier density and mobility in a way that was described for the first time by Kostlin in ITO [1]. In general, for a material to be transparent across the visible

spectrum, its band gap must be greater than 3 eV to enable transmission up to the near UV (0.4  $\mu\text{m}$ ) wavelength, and its free carrier plasma resonance absorption must lie in the near-infrared (1.5  $\mu\text{m}$ ) or longer wavelengths. Increasing carrier density decreases resistivity but also has the drawback of shifting the IR absorption edge toward the visible, thus narrowing the transmission window. This shift at the IR end of the spectrum is determined by the plasma oscillation of the free carriers that screens the incident electromagnetic wave via intraband transitions within the conduction band. The characteristic wavelength ( $\lambda_p$ ) for IR reflection in transparent conducting oxides is well predicted by the Drude model [2]. The position of the UV edge is dependent, in part, on the free carrier density in the material. Straightforward analysis of the density of states in the conduction band reveals that the UV edge will shift to shorter wavelengths with increasing carrier density ( $n$ ) because the change in the optical band gap ( $\Delta E$ ) increases with carrier density as  $\Delta E \sim n^{3/2}$  up to a certain value [3, 4]. Further increase of carrier concentration leads an initial band gap shrinkage with a somewhat different behavior for the subsequent change in the optical band gap, due to a merge between the conduction band edge and the dopant band derived from the high level of extrinsic dopants added to the film [5,6].

### References

- [1] H. Kostlin, R. Jost, W. Lems, *Phys. Stat. Sol. A*, 29 (1975) 87.
- [2] P. Drude, *Phys. Z.*, 1 (1900) 30.
- [3] E. Burstein, *Phys. Rev.*, 93 (1954) 632.
- [4] T. S. Moss, *Proc. Phys. Soc. London, Ser. B* 67 (1964) 775.
- [5] A. P. Roth, J. B. Webb, D. F. Williams, *Solid State Commun.*, 39 (1981) 1269.
- [6] A. P. Roth, J. B. Webb, D. F. Williams, *Phys. Rev. B*, 25 (1982) 7836.

### 3.3. Electrical Properties

From the discussion on section 3.1, it follows that transport properties of electrical carriers in thin film materials must be severely affected by the various structural aspects. We must expect to see the open-circuit voltage, the short-circuit current and the fill factor to be, as a consequence, influenced by this change in the electrical properties of the films. The major electrical parameters that can be affected are the diffusion length, mobility and related to this one, the carrier density. Some effects in close connection with this changes are the measurement of the electrical properties of thin films such as Hall effect and Seebeck coefficient. Finally, even if it does not seem to be an electrical effect, the presence of defects are closely related to this one.

#### 3.3.1. Diffusion Length

Diffusion length is one of the most important parameters influencing the electrical performance of any thin film device. The diffusion length  $L$  is given by  $L = (kT\tau\mu/e)^{1/2}$ , where  $k$  is the Boltzmann constant, showing that mobility and recombination lifetime fundamentally control  $L$ . Lifetime controlling mechanisms such as grain boundary, interface, and surface recombination have already been

discussed in sections 3.1.3, 3.1.4 and 3.1.8, and each will cause a change in the effective diffusion length. Quite generally diffusion length should be as long as possible in order to assure a minimum impact of the carrier scattering.

#### 3.3.2. Mobility

Lattice scattering generally dominates the mobility in pure materials, but in thin films grain boundary scattering can significantly affect the observed mobility. The mobility measured across or parallel to grain boundaries can be significantly different [1]. Thus mobility of any layer can be both an important parameter controlling cell performance and very difficult to measure in real devices. Further complications arise as a result of impurity concentrations and gradients which also affect mobility and hence diffusion length.

It is worth noting that, in the particular case of transparent conducting oxides, as they act as electrode in PV cells, electrical carriers must flow in both directions, perpendicular and parallel to the interface, when traveling to the grid. This mean a tradeoff between the optimal preferential growth of the grains and the best electrical properties allowing good carrier mobility to the grid. Columnar grain growth perpendicular to the surface of the cell, with grains having very small cross section, could represent a significant number of scattering effects along the path between the window material and the grid. If columnar grain growth proceeds parallel to the surface of the cell, transport through the grid could be enhanced, but light scattering to normal incident light could be affected by the increased number of interfaces between grains, if its cross section is not big enough.

#### 3.3.2. Defects

We have already mentioned in section 3.1 the fact that defects can act as trapping and recombination centers. But there are some kind of defects that should intentionally been introduced, in order to enhance electrical properties of the films. These kind of defects are generally know as dopants. A dopant must not be considered as an impurity, as previously mentioned in section 3.1.6.

Oxides with a fundamental band gap of 3 eV of more are insulators at room temperature in the stoichiometric undoped state. This condition is hardly achieved in real metal oxides grown by any thin film process. Unintentional dopants are either added or created that generally confer to the film a  $n$ -type conductivity. Nevertheless, the level of doping obtained in this way is so small, that the conductivity of metal oxide thin films without intentional doping are not useful for practical applications like transparent conducting oxides. To become highly conductive, the oxide must be doped to degeneracy by increasing the free carrier density enough to move the Fermi level into the conduction band in  $n$ -type materials (or into the valence band, in the case of  $p$ -type materials). Degenerate doping requires a source of electron donors (or hole acceptors) in the form of point defects (often oxygen vacancies in the  $n$ -type materials) or impurities with an ionization energy close to the conduction (valence) band; this severely limits the selection of transparent conducting oxide materials. In some oxides –in particular those with  $d^{10}$  cations such as  $\text{In}_2\text{O}_3$ ,  $\text{ZnO}$ ,  $\text{SnO}_2$  and  $\text{CdO}$ – native

stoichiometric point defects like oxygen vacancies are readily ionized and thereby donate electrons to the conduction band. Further doping is usually required (for example Al in zinc oxide, Sn in indium oxide and F in tin dioxide), and these dopants must find substitutional sites in the lattice. This high level of ionized dopants in the form of charged native point defects or impurity atoms typically leads to a decrease in carrier mobility ( $\mu$ ) and represents a tradeoff when optimizing the resistivity of the material.

Extrinsic dopants in the form of intentionally added impurities can be either cationic (for example  $\text{Sb}^{5+}$  substitutionally on the tetra-valent Sn site in  $\text{SnO}_2$ ) or anionic (F substitutionally on an O site in ZnO). It is important to point out that the native stoichiometric point defects like these oxygen vacancies are not mobile at room temperature, and hence ionic conduction does not play a role in the conductivity of transparent conducting oxide materials at room temperature. Furthermore, all practical transparent conductors in use today are degenerately doped  $n$ -type with either intentionally added dopants or native point defects created through non stoichiometric deposition conditions. There is no currently  $p$ -type transparent conducting oxides in practical thin film solar cells.

#### References

- [1] Lawrence L. Kazmerski, "Polycrystalline and Amorphous Thin Films and Devices", Chap.3, Academic Press, New York, 1980.

#### 4. Transparent Conducting Oxides: Selected Materials for thin Film Solar Cells

It was Bädecker who first reported in 1907 on a kind of transparent conducting oxide, by using a primitive vapor deposition system to obtain CdO in thin film form that was both optically transparent and electrically conductive [1]. Since then there have been mainly three oxides that have become the most important ones for commercial applications as transparent conductors: tin oxide, indium oxide and zinc oxide. The properties that made them of interest for photovoltaic applications will be discussed in some detail in the next sections. By volume, the most deposited transparent conducting oxide is tin dioxide, which is mainly used in IR-efficient architectural window applications. The indium oxide materials are the highest performance and best-understood materials in the transparent conducting oxide class. Zinc oxide, like tin oxide, is also primarily currently used in window coatings (e. g., multilayer stacks with Ag). However recent processing-related performance improvements and low cost make it an attractive replacement for high-cost indium-based oxide material.

#### References

- [1] K. Bädecker, Ann. Phys. (Leipzig), 22 (1907) 749.

##### 4.1 Tin Dioxide ( $\text{SnO}_2$ )

The TCO that is deposited in the largest quantity (by area) and that may be of the greatest economic importance is  $\text{SnO}_2$

doped with F or Sb. This material is used widely for energy-efficient windows in architectural applications. The advantages of  $\text{SnO}_2$  are that it is inexpensive both in terms of raw materials and processing, because it can be easily deposited using chemical (rather than vapor-phase) methods such as spray pyrolysis from the chlorides or from organometallic precursors. It is receiving more attention for PVs, especially for the heterojunction with intrinsic thin layer (HIT) cells and related cells (such as amorphous or microcrystalline Si) when deposited from sources with low decomposition temperatures. F:  $\text{SnO}_2$  deposited from  $\text{SnCl}_2$  precursors typically [1] has the cassiterite structure (similar to rutile) with a direct gap of 4.0 eV and an indirect gap of 2.6 eV. Films doped with fluorine show [2] an increase in the gap to 4.1 eV and the best resistivities on the order of  $6 \times 10^{-4} \Omega\text{cm}$ , mobilities of  $20 \text{ cm}^2/\text{Vs}$ , and carrier concentrations of  $5\text{--}8 \times 10^{20} \text{ cm}^{-3}$ ; Sb-doped films show similar properties. Conductivities for  $\text{SnO}_2$ -based materials are not as good for ITO, and process temperatures for the best  $\text{SnO}_2$ -based materials are around  $450^\circ\text{C}$ , limiting their use in many PV technologies.

#### References

- [1] J. Dutta, J. Perrin, T. Emeraud, J.-M. Laurent, and A. Smith, *J. Mater. Sci.*30, 53-62 (1995).  
[2] E. Elangovan and K. Ramamurthi, *Cryst. Res. Technol.*38, 779-784 (2003).

##### 4.2. Indium Oxide ( $\text{In}_2\text{O}_3$ )

The TCOs most widely used for display applications are crystalline ITO (c-ITO), amorphous ITO (a-ITO), and amorphous IZO (a-IZO). The most common method for the deposition of these TCOs is dc/rf magnetron sputter deposition.

In general, ITO is deposited from sintered ceramic  $\text{In}_2\text{O}_3$  targets containing between 3 wt% and 10 wt%  $\text{SnO}_2$ , whereas IZO targets contain 7–10 wt% ZnO. At present, crystalline ITO deposited onto substrates heated to  $250\text{--}350^\circ\text{C}$  offers the lowest resistivity currently available ( $1\text{--}3 \times 10^{-4} \Omega\text{cm}$ ). Two alternatives to c-ITO that may be processed at room temperature are a-ITO and a-IZO. Both of these amorphous materials have slightly inferior electrical transport properties compared with c-ITO, but they are, in some applications, favored over crystalline ITO because they offer improved lithographic line definition due to the more controllable wet-etch characteristics of the amorphous phase. In addition, a-IZO offers the advantage of not requiring the addition of oxygen to the sputter gas, because the optimum resistivity is at or near zero oxygen partial pressure.

When appropriately doped, both ZnO and  $\text{In}_2\text{O}_3$  are useful transparent conductors. The cation coordination and consequently the crystal structures of these oxides are, however, quite different, and their mutual solid solubility is low. Across a wide range of ZnO-rich compositions, the  $\text{In}_2\text{O}_3\text{--ZnO}$  phase diagram [1] shows that these two oxides react to form a set of homologous compounds enabling the two cations to preserve their individual tetragonal (wurtzite) or octahedral (bixbyite) coordination [2]. However, in a

wide range of compositions, the tendency of Zn and In oxides to preserve their four and six (respectively) oxygen coordination has the effect of frustrating the crystallization, resulting in amorphous materials with remarkable thermal stability. The amorphous alloys of IZO (In<sub>2</sub>O<sub>3</sub>-10wt% ZnO) would require diffusion-limited phase separation for crystallization and, as a consequence, a-IZO remains amorphous even when annealed to temperatures above 500°C.

## References

- [1] T. Moriga, D. D. Edwards, T. O. Mason, G. B. Palmer, K. R. Poepelmeier, C. R. Kannewurf, and I. Nakabayashi, *J. Am. Ceram. Soc.* 81 1310-1316 (1998).
- [2] P. J. Cannard and R. J. D. Tilley, *J. Solid State Chem.* 73 418-426 (1988).

### 4.3. Zinc Oxide (ZnO)

Zinc oxide (ZnO) belongs to the group of transparent conductive oxides (TCO) like the compound semiconductors indium oxide (In<sub>2</sub>O<sub>3</sub>) and tin dioxide (SnO<sub>2</sub>) [1]. These materials possess a wide energy band gap ( $E_g > 3.4$  eV) and are therefore transparent in the wavelength region from about 350 to 800 nm, where the long wavelength cutoff depends on the charge carrier concentration. TCO films can be prepared with resistivity in the region of 1 to  $5 \times 10^{-4}$  Ωcm, only one to two orders of magnitude higher than typical metals ( $\rho_{Cu} = 1.7$  μΩcm,  $\rho_{Mo} = 5.4$  μΩcm,  $\rho_{Pb} = 21$  μΩcm). This makes these materials very well suited for transparent electrodes in flat panel displays (liquid crystal, electroluminescence and plasma displays), thin film solar cells, microwave oven windows, low emissivity glass, thermal solar collectors, etc. In the last few years zinc oxide has gained increasing attention as a TCO material because of the higher abundance compared to the other TCO materials. Another advantage of zinc oxide is its stability in hydrogen containing atmospheres [2], e.g., in a silan (SiH<sub>4</sub>) plasma discharge, which is used for the preparation of a-Si:H thin film solar cells [3]. Recently, zinc oxide single crystals [4] of high quality have been prepared. Such crystals are promising candidates as substrates for gallium nitride epitaxial films for blue laser applications. Moreover, zinc oxide itself has been investigated as a material for blue lasers due to its direct band gap [5, 6].

Until now the research in the field of TCO films has been performed on an empirical basis, which is not surprising taking into account that the doping mechanism even in single crystalline zinc oxide (and other TCO materials) is not yet clear [7]. Also the theoretical understanding of other heavily doped semiconductors, even silicon, is poor [8, 9]. In view of the fact, that the resistivity of TCO films has reached a limit around  $10^{-4}$  Ωcm, attempts have been made in the last years to develop new ternary TCO materials [10–12] in order to surmount this limit. As typical representatives of compound semiconductors these oxides can be made conductive by intrinsic (defects) or extrinsic (dopants) charge carriers.

Zinc oxide crystallizes in the hexagonal wurtzite-type structure. It has a polar hexagonal axis, the c axis, chosen to

be parallel to z direction. The point group is in the various notations 6mm or  $C_{6v}$ , the space group is  $P6_3mc$  or  $C_{6v}^4$ . One zinc ion is surrounded tetrahedrally by four oxygen ions and vice versa. The primitive unit cell contains two formula units of ZnO. The ratio  $c/a$  of the elementary translation vectors, with values around 1.60, deviates slightly from the ideal value  $c/a = (8/3)^{1/2} = 1.6333$ . In contrast to other II<sup>b</sup>-VI semiconductors, which exist both in the cubic zinc blende and the hexagonal wurtzite-type structures (like ZnS, which gave the name to both structures), ZnO crystallizes with great preference in the wurtzite-type structure. The cubic zinc blende-type structure can, to some extent, be stabilized by epitaxial growth of ZnO on suitable cubic substrates, while the rock salt structure is stable only under pressure [17]. The tetrahedral coordinated diamond, zinc blende, and wurtzite-type crystal structures are characteristic for covalent chemical binding with sp<sup>3</sup> hybridization. While the Group IV element semiconductors like diamond, silicon and germanium have completely covalent bonding, one has an increasing admixture of ionic binding when going from the Group IV over the III-V and II<sup>b</sup>-VI to the I<sup>b</sup>-VII semiconductors, ending with completely ionic binding for the II<sup>a</sup>-VI and I<sup>a</sup>-VII insulators like MgO or NaCl, which frequently crystallise in the rock salt structure.

Intrinsic zinc oxide single crystals have typical resistivity in the range of 1–10 Ωcm [4, 14]. However, *Korimako et al.* [15] reported dark resistivity of up to  $\approx 10^{12}$  Ωcm for lithium compensated ZnO crystals by annealing at 1070 K in a Li<sub>2</sub>CO<sub>3</sub> melt. The low resistivity at room temperature which is required for the application of TCO films as transparent electrodes can be achieved in two ways:

- creation of intrinsic donors by lattice defects (for instance oxygen vacancies or metal atoms on interstitial lattice sites) or
- introduction of extrinsic dopants (either metals with oxidation number three on substitutional metal lattice sites or halogens with oxidation number minus one on oxygen lattice sites).

The first possibility can be realized during the deposition by carefully adjusting the oxygen partial pressure and deposition rate. The other way is a reduction process of the oxide after deposition, for instance by annealing in vacuum or in a hydrogen containing atmosphere [16]. However, it has been found that such films exhibit properties are not well suited for practical applications. First, the resistivity is only about  $10^{-2}$  to  $10^{-3}$  Ωcm. Furthermore, these films are not stable at ambient conditions (especially at higher temperatures) due to the reoxidation of the oxygen deficient films. Therefore, in most cases extrinsic dopants are added during the deposition. In reality in doped oxide films both doping mechanisms occur simultaneously. By increasing the oxygen partial pressure during (or after) preparation the dopants become oxidized and hence lose its doping effect. Another complication arises due to the variation of phases, structure and morphology when changing the deposition parameters, especially the oxygen partial pressure. Actually, ZnO films (as well as other TCO films) are phase mixtures containing not only the desired phase (e. g., ZnO) but also secondary phases, like gahnite (ZnAl<sub>2</sub>O<sub>4</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) or ZnO<sub>2</sub>, a low temperature phase in the Zn-O system.

Normally, these additional phases which of course contribute to the electronic and structural–mechanical film properties are not detected by standard analytical techniques like X-ray diffraction patterns and photoelectron spectroscopy due to their low concentrations. These phases were recently identified in aluminium-doped zinc oxide by transmission electron microscopy (TEM) and selected area electron diffraction (SAD) [17]. *Minami et al.* [11] reported the doping of zinc oxide by adding elements like Y, Zr, Ti and Hf, which do not exhibit an additional valence electron like the more common dopants B, Al, Ga or In. Nevertheless, *Minami et al.* obtained resistivity in the low  $10^{-4}$   $\Omega\text{cm}$  range. This observation is somewhat puzzling with respect to the conventional explanation of extrinsic doping (see above). However, by assuming that these oxide forming additives could attract oxygen from the zinc oxide lattice, thus generating oxygen vacancies, the doping would be actually caused by oxygen vacancies.

Concerning the application of zinc oxide and other TCO materials as transparent electrodes in displays and thin film solar cells the question arises, what the lower limit of the resistivity of such degenerate semiconducting thin solid films. The well known reviews about TCO materials [1, 11, 12, 18] do not address the physical limits of the resistivity. *Bellingham et al.* [19] applied the ionized impurity scattering model of *Brooks and Herring et al.* [20], *Dingle et al.* [21] and *Moore et al.* [22] to TCO films. They came to the conclusion that ionized impurities govern the transport for carrier densities above  $10^{19}$   $\text{cm}^{-3}$ . *Bellingham et al.* [19] estimated a limiting carrier mobility of  $90 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for the three mentioned TCO materials. *Minami et al.* [11, 23] combined scattering at grain boundaries and ionized impurity scattering to explain their results on selfdoped and extrinsically (B, Al, Ga) doped ZnO films. In the region  $n > 10^{20}$   $\text{cm}^{-3}$  the experimental data could be described only by taking into account a very strong non-parabolicity of the zinc oxide conduction band. With respect to the theoretical scattering models, it is not really clear which charge state of the dopant has to be used in the calculations. For extrinsic dopants on cation lattice places, the charge state should be  $Z=1$ , while oxygen vacancies exhibit a charge state  $Z = 2$ , leading to lower mobility.

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#### Conflict of interest

The authors declare that there is no conflict of interest in the current article.

#### References

- [1] H. L. Hartnagel, A. L. Dawar, A. K. Jain, C. Jagadish, 1995 *Semiconducting Transparent Thin Films* (Bristol: Institute of Physics Publishing).
- [2] T. Minami, H. Sato, H. Nanto, S. Takata, *Thin Solid Films* 171 (1989) 277-290.
- [3] C. Beneking, B. Rech, S. Wieder, O. Kluth, H. Wagner, W. Frammelsberger, R. Geyer, P. Lechner, H.

- Rübel, H. Schade, *Thin Solid Films* 351 (1999) 241-249.
- [4] D. C. Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, C. W. Litton, G. Cantwell, W. C. Harsch, *Solid State Commun.* 105 (1998) 399-401.
- [5] K. Iwata, P. Fons, A. Yamada, K. Matsubara, S. Niki, *J. Cryst. Growth* 209 (2000) 526-531.
- [6] Y. R. Ryu, S. Zhu, D. C. Look, J. M. Wrobel, H. M. Jeong, H. W. White, *J. Cryst. Growth* 216 (2000) 330-334.
- [7] D. C. Look, J. W. Hemsky, J. R. Sizelove, *Phys. Rev. Lett.* 82 (1999) 2552-2555.
- [8] D. B. M. Klaassen, *Solid-State Electron.* 35 (1992) 961-967.
- [9] A. Schenk, *J. Appl. Phys.* 79 (1996) 814-831.
- [10] X. Wu, T. J. Coutts, W. P. Mulligan, *J. Vac. Sci. Technol. A* 15 (1997) 1057-1062.
- [11] T. Minami, *MRS Bull.* 25 (2000) 38-44.
- [12] A. J. Freeman, K. R. Poepfelmeier, T. O. Mason, R. P. H. Chang, T. J. Marks, *MRS Bull.* 25 (2000) 45-51.
- [13] F. C. M. van de Pol, F. R. Blom, Th. J. A. Popma *Thin Solid Films* 204 (1991) 365-376.
- [14] E. Ziegler, A. Heinrich, H. Oppermann, G. Stöver, *Phys. Status Solidi A* 66 (1981) 635-648.
- [15] I. B. Kobiakov, *Solid State Commun.* 35 (1980) 305-310.
- [16] O. Caporaletti, *Solar Energy Mater.* 7 (1982) 65-73.
- [17] I. Sieber, N. Wanderka, I. Urban, I. Dörfel, E. Schierhorn, F. Fenske, W. Fuhs, *Thin Solid Films* 330 (1998) 108-113.
- [18] K. L. Chopra, S. Major, D. K. Pandya, *Thin Solid Films* 102 (1983) 1-46.
- [19] J. R. Bellingham, W. A. Phillips, C. J. Adkins, *J. Mater. Sci. Lett.* 11 (1992) 263-265.
- [20] H. Brooks, *Adv. Electr. Electron Phys.* 7 (1955) 85-182.
- [21] R. B. Dingle, *Phil. Mag.* 46 (1955) 831-852.
- [22] E. J. Moore, *Phys. Rev.* 160 (1967) 618-626.