

Handbook of
Nanostructured Thin Films and Coatings

Organic Nanostructured Thin Film Devices and Coatings for Clean Energy



Edited by
Sam Zhang

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Preface

The twenty-first century is said to be the century of nanotechnologies. In a way, it is. The development of science and technology has come to a stage where “microscopic” is no longer enough to properly describe or depict a scientific phenomenon or a technological process. With the advance of nanoscience and nanotechnology, the world technological landscape changes not only affect the way scientists do research, technologists carry out development, and engineers manufacture products, but also the way ordinary people go about their daily life, through, for instance, nanomedicine, cell phones, controlled drug delivery, no-pain operations, solar cell-powered gadgets, etc. Thin films and coatings play a very important and indispensable role in all of these. This three-volume book set aims to capture the development in the films and coatings area in relation to nanoscience and nanotechnology so as to provide a timely handbook series for researchers to refer to and for newcomers to learn from, and thus contribute to the advancement of the technology.

The three-volume book set, *Handbook of Nanostructured Thin Films and Coatings*, has 25 chapters where 11 chapters in volume 1 concentrate on the mechanical properties (hardness, toughness, adhesion, etc.) of thin films and coatings, including processing, properties, and performance, as well as a detailed analysis of theories and size effect, etc., as listed here: Chapter 1, The Fundamentals of Hard and Superhard Nanocomposites and Heterostructures; Chapter 2, Determination of Hardness and Modulus of Thin Films; Chapter 3, Fracture Toughness and Interfacial Adhesion Strength of Thin Films: Indentation and Scratch Experiments and Analysis; Chapter 4, Toughness and Toughening of Hard Nanocomposite Coatings; Chapter 5, Processing and Mechanical Properties of Hybrid Sol-Gel-Derived Nanocomposite Coatings; Chapter 6, Using Nanomechanics to Optimize Coatings for Cutting Tools; Chapter 7, Electrolytic Deposition of Nanocomposite Coatings: Processing, Properties, and Applications; Chapter 8, Diamond Coatings: The Industrial Perspective; Chapter 9, Amorphous Carbon Coatings; Chapter 10, Transition Metal Nitride-Based Nanolayered Multilayer Coatings and Nanocomposite Coatings as Novel Superhard Materials; and Chapter 11, Plasma Polymer Films: From Nanoscale Synthesis to Macroscale Functionality.

Volume 2 contains eight chapters focusing on functional properties, i.e., optical, electronic, and electrical properties, and the related devices and applications: Chapter 1, Large-Scale Fabrication of Functional Thin Films with Nanoarchitecture via Chemical Routes; Chapter 2, Fabrication and Characterization of SiC Nanostructured/Nanocomposite Films; Chapter 3, Low-Dimensional Nanocomposite Fabrication and its Applications; Chapter 4, Optical and Optoelectronic Properties of Silicon Nanocrystals Embedded in SiO₂ Matrix; Chapter 5, Electrical Properties of Silicon Nanocrystals Embedded in Amorphous SiO₂ Films; Chapter 6, Properties and Applications of Sol-Gel-Derived Nanostructured Thin Films: Optical Aspects; Chapter 7, Controllably Micro/Nanostructured Films and Devices; and Chapter 8, Thin Film Shape Memory Alloy for Microsystem Applications.

Volume 3 focuses on organic nanostructured thin-film devices and coatings for clean energy with six chapters discussing the processing and properties of organic thin films, devices, and coatings for clean energy applications: Chapter 1, Thin Film Solar Cells Based on the Use of Polycrystalline Thin Film Materials; Chapter 2, Anodized Titania Nanotube Array and its Application in Dye-Sensitized Solar Cells; Chapter 3, Progress and Challenges of Photovoltaic Applications of Silicon Nanocrystalline Materials; Chapter 4, Semiconductive Nanocomposite Films for Clean Environment; Chapter 5, Thin Coating Technologies and Applications in High-Temperature Solid Oxide Fuel Cells; and Chapter 6, Nanoscale Organic Molecular Thin Films for Information Memory Applications.

A striking feature of these books is that both novice and experts have been considered while they were written: the chapters are written in such a way that for newcomers in the relevant field, the handbooks would serve as an introduction and a stepping stone to enter the field with least confusion, while for the experts, the handbooks would provide up-to-date information through the figures, tables, and images that could assist their research. I sincerely hope this aim is achieved.

The chapter authors come from all over the globe: Belgium, China, the Czech Republic, Egypt, Germany, India, Korea, Singapore, Taiwan, the Netherlands, the United Kingdom, and the United States. Being top researchers at the forefront of their relevant research fields, naturally, all the contributors are very busy. As editor, I am very grateful that they all made special efforts to ensure timely response and progress of their respective chapters. I am extremely indebted to many people who accepted my request and acted as reviewers for all the chapters—as the nature of the writing is to cater to both novice and experts, the chapters are inevitably lengthy. To ensure the highest quality of the chapters, more than 50 reviewers (at least two per chapter) painstakingly went through all the chapters and came out with sincere and frank criticism and suggestions that helped make the chapters complete. Though I am not able to list all the names, I would like to take this opportunity to say a big thank you to all of them. Last but not least, I would like to convey my gratitude to many CRC Press staff, especially Allison Shatkin and Jennifer Ahringer at Taylor & Francis Group, for their invaluable assistance rendered to me throughout the entire endeavor that made the smooth publication of the handbook set a reality.

Sam Zhang
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Editor



Sam Zhang Shanyong, better known as Sam Zhang, received his BEng in materials in 1982 from Northeastern University (Shenyang, China), his MEng in materials in 1984 from the Central Iron and Steel Research Institute (Beijing, China), and his PhD in ceramics in 1991 from the University of Wisconsin-Madison (Madison, Wisconsin). Since 2006, he has been a full professor at the School of Mechanical and Aerospace Engineering, Nanyang Technological University (Singapore).

Professor Zhang serves as editor in chief for *Nanoscience and Nanotechnology Letters* (United States) and as principal editor for the *Journal of Materials Research* (United States), among other editorial commitments for international journals. He has been involved in the fields of processing and characterization of thin films and coatings for the past 20 years, his interests ranging from

hard coatings to biological coatings and from electronic thin films to energy films and coatings. He has authored/coauthored more than 200 peer-reviewed international journal articles, 14 book chapters, and guest-edited 9 journal volumes in *Surface and Coatings Technology* and *Thin Solid Films*. Including this handbook, he has authored and/or edited 6 books so far: *CRC Handbook of Nanocomposite Films and Coatings: Vol. 1, Nanocomposite Films and Coatings: Mechanical Properties*; Vol. 2, *Nanocomposite Films and Coatings: Functional Properties*; Vol. 3, *Organic Nanostructured Film Devices and Coatings for Clean Energy*, and *Materials Characterization Techniques* (Sam Zhang, Lin Li, Ashok Kumar, published by CRC Press/Taylor & Francis Group, 2008); *Nanocomposite Films and Coatings—Processing, Properties and Performance* (edited by Sam Zhang and Nasar Ali, Published by Imperial College Press, U.K., 2007), and *CRC Handbook of Biological and Biomedical Coatings* (scheduled for a 2010 publication by CRC Press/Taylor & Francis Group).

Professor Zhang is a fellow at the Institute of Materials, Minerals and Mining (U.K.), an honorary professor at the Institute of Solid State Physics, Chinese Academy of Sciences, and a guest professor at Zhejiang University and at Harbin Institute of Technology. He was featured in the first edition of *Who's Who in Engineering Singapore* (2007), and featured in the 26th and 27th editions of *Who's Who in the World* (2009 and 2010). Since 1998, he has been frequently invited to present plenary keynote lectures at international conferences including in Japan, the United States, France, Spain, Germany, China, Portugal, New Zealand, and Russia. He is also frequently invited by industries and universities to conduct short courses and workshops in Singapore, Malaysia, Portugal, the United States, and China.

Professor Zhang has been actively involved in organizing international conferences: 10 conferences as chairman, 12 conferences as member of the organizing committee, and 6 conferences as member of the scientific committee. The Thin Films conference series (The International Conference on Technological Advances of Thin Films & Surface Coatings), initiated and, since, chaired by Professor Zhang, has grown from 70 members in 2002 at the time of its inauguration to 800 in 2008. It has now become a biannual feature at Singapore.

Professor Zhang served as a consultant to a city government in China and to industrial organizations in China and Singapore. He also served in numerous research evaluation/advisory panels in Singapore, Israel, Estonia, China, Brunei, and Japan. Details of Professor Zhang's research and publications are easily accessible at his personal Web site: <http://www.ntu.edu.sg/home/msyzhang>.

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*R.W. Miles, G. Zoppi, K.T. Ramakrishna Reddy,
and I. Forbes*

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1.1 INTRODUCTION

As shown in Figure 1.1, most solar cells produced and sold at the present time are based on the use of crystalline or multi-crystalline silicon [1]. Despite the excellent progress in developing these technologies, it has been realized for some time that there is a need to reduce production costs significantly to compete directly with other forms of power generation. This need for solar cells and modules to be produced with much lower manufacturing costs has been the major impetus for developing thin film solar cells [2–6].

Crystalline and multi-crystalline silicon have indirect energy bandgaps, with correspondingly low optical absorption coefficients, such that several hundred microns of silicon are needed to

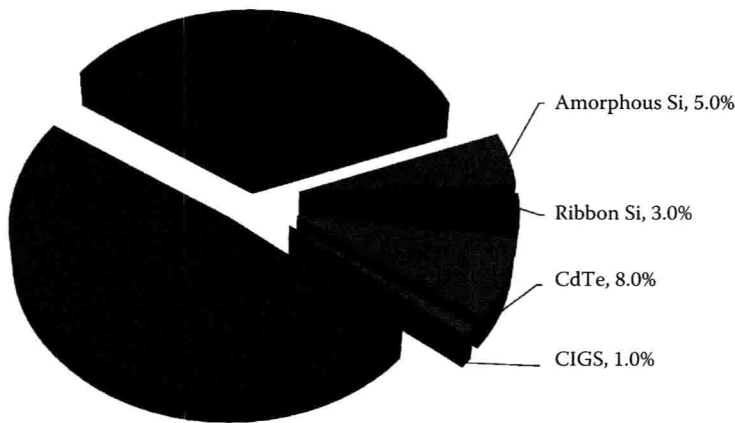


FIGURE 1.1 The market share of PV cell types sold during 2008.

absorb most of the incident light. Carriers generated by the incident light must also diffuse to the junction region to be acted upon by the electric field at the junction to contribute to the power generated. For the “minority carrier diffusion length” to be comparable or greater than the “optical absorption depth,” recombination centers in the silicon must be minimized by

1. Purifying the silicon to a high level
2. Producing the silicon with as few crystal defects as possible

Silicon solar cells are costly because of

1. High material usage
2. High processing costs (to purify the material and minimize crystal defects)
3. High “handling costs” in the manufacturing process, as often the processing is not fully automated

Thin film solar cells based on the use of direct-energy-bandgap semiconductors, e.g., hydrogenated amorphous silicon (α Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS), minimize these costs because their correspondingly high optical absorption coefficients ($\alpha > 10^4 \text{ cm}^{-1}$) mean that only a few microns of material are needed to absorb the incident sunlight. This means that a long minority carrier diffusion length is not required, because most of the photo-carriers are generated within the depletion region or very near to the edge of the depletion (usually, $< 1 \mu\text{m}$). This means that relatively low-cost methods can be used to make devices. Furthermore, depositing thin films of materials lends itself naturally to continuous production processes that are capable of depositing large areas of material.

The most successful materials used for making photovoltaic (PV) solar cells in the thin film form are α Si:H, CdTe, CIGS, and CuInS_2 (copper indium disulfide). Despite the continuing success of deploying α Si:H devices over the past decade, it should be noted that the efficiencies of commercially produced single-junction α Si:H modules are low ($< 4\%$) due to the light-induced degradation of efficiency, due to the Staebler–Wronski effect [7]. More complex structures, such as double junction, triple junction, and micromorph tandem devices, have been developed to improve efficiency and stability [7]. However, the very best devices produced only have efficiencies of around 10% and the complexity of manufacturing increases device fabrication costs.

This chapter will concentrate on the much more efficient, stable solar cells made using CdTe, CIGS, and CuInS_2 . Some novel inorganic absorber-layer materials that are currently of interest are also discussed. These include CuInAlSe_2 , $\text{Cu}_2\text{ZnSn}(\text{Se},\text{S})_4$, and SnS (tin monosulfide).

Currently, the largest manufacturer of CdTe-based solar cells is the U.S. company, First Solar. First Solar manufactures modules with efficiencies approaching 10% with a cost of 0.74 €/W. The CdTe modules are approximately 15% cheaper for each kW installed than their nearest rivals. Despite needing a larger area to generate the same amount of power, the cost advantage has persuaded many to buy CdTe-based modules [8]. Recent projects include the integration of CdTe modules onto a Logistics Building of a U.S. Army base in Ramstein, Germany (so far the biggest example of building-integrated photovoltaics [BIPV] using a thin film technology), and the fabrication of a large solar power station in Muldentalkreis, Saxony, and Germany. First Solar is currently building four further production facilities in Malaysia (joint capacity of 480 MW) and one further production facility in Frankfurt (Oder), Germany (120 MW facility) [8].

Other companies that have been involved in developing pilot production lines for the manufacture of CdTe-based modules include Matsushita (screen printing), BP Solar (electrodeposition), and Antec GmbH (close-spaced sublimation [CSS]). Although these companies had good success in producing small-area cells with good efficiencies, all these companies have now ceased production. This has partly been because of concerns with the lack of public acceptability of using a toxic metal such as cadmium in a “green product.” This is despite detailed studies having shown that the environmental costs are no worse than those with other methods of energy production [4]. It can in fact be argued that combining cadmium (a highly toxic by-product of the extraction of zinc and copper) with tellurium to form CdTe, a nontoxic compound, that can be used to produce “green electricity,” is environmentally beneficial. The impressive success of First Solar in selling its products into Germany, one of the most environmentally sensitive countries in the world, suggests that CdTe technology is becoming increasingly acceptable to the general public. Table 1.1 gives the capacity and output of First Solar and a new German company, Calyxo, during the period 2007–2008.

Table 1.2 lists the main producers of chalcopyrite-based (CIGS and CuInS₂) solar modules during 2007–2008. It is clearly evident that there are many more manufacturers than for CdTe-based cells and modules. This is because the chalcopyrite solar cells and modules can be made totally Cd free, minimizing environmental concerns. Most of these manufacturers use CIGS as the absorber-layer material. The exceptions are Sulphurecell and Odersun, who use copper indium disulfide. In the laboratory, CIGS-based cells have been produced with efficiencies up to 19.9% using the co-evaporation method [9], just lower in efficiency than the best cells made using multi-crystalline silicon. However, transferring the excellent results obtained in the laboratory into low-cost modules with acceptable efficiencies and yields has proved challenging. The best manufacturing costs are about 2.5 €/Wp, i.e., at present comparable to multi-crystalline silicon [8]. However, it is expected that with economies of scale, the situation will reverse over the next decade. There are currently concerns with respect to the lack of abundance of indium and gallium. This is pushing up the price of the raw materials to very high levels and may limit the large-scale deployment of CIGS-based modules in the longer term. It is however expected that these elements could be replaced by other elements that are more available and cheaper, e.g., Sn and Zn or Al. Work is already ongoing into trying to develop such materials. Figure 1.2 shows an example of BIPV, the 85 kWp Technium

TABLE 1.1
Companies Manufacturing CdTe Modules during 2007–2008

Company	Country	2007 Capacity (MW)	2007 Production (MW)	2008 Capacity (MW)	2008 Production (MW)
Calyxo	Germany	8	1	25	5
First Solar	United States	210	100	210	200

Source: Rentzing, S., *New Energy*, 3, 58, 2008.

TABLE 1.2
Companies Manufacturing Chalcopyrite Modules during 2007–2008

Company	Country	2007 Capacity (MW)	2007 Production (MW)	2008 Capacity (MW)	2008 Production (MW)
Avancis	Germany			20	1
Day Star Technologies	United States			25	1
Global Solar	United States	3	3	75	75
Honda Soltec	Japan	27.5	0	27.5	20
Johanna Solar	Germany			30	3
Odersun	Germany	4.5	1	30	1
Nano Solar	United States	430	0	430	1
Scheuten	The Netherlands	10	3	40	10
Showa Shell Sekiyo	Japan	20	10	20	20
Solibro	Germany			25	1
Sulphurcell	Germany	5	1	5	2
Würth Solar	Germany	15	15	30	30
VHF Technologies	Switzerland	2	0.1	25	5

Source: Rentzing, S., *New Energy*, 3, 58, 2008.

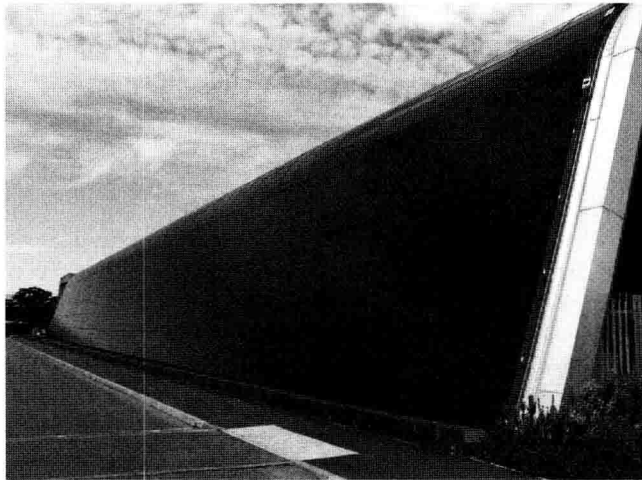


FIGURE 1.2 The 85 kWp Technium OptIC building in St Asaph, Wales, which is covered with the of CIGS modules manufactured by Shell Solar.

OptIC (Opto-electronics Technology and Incubation Centre) in St Asaph, Wales, United Kingdom, which is covered with the CIGS modules manufactured by Shell Solar.

The thin film solar cells and modules made using CdTe are usually formed by sequentially depositing layers onto glass substrates in the following sequence: transparent conductive oxide (TCO), buffer layer, absorber layer, and finally the back-contact layer. This structure, in which the TCO layer is deposited first and the back-contact layer last, is known as the “superstrate configuration.” The thin film solar cells and modules made using the chalcopyrite compounds are usually formed by sequentially depositing layers onto glass substrates in the following sequence: back contact,

absorber layer, buffer layer, TCO, and finally the top grid contact, and are referred to as being in the “substrate configuration.”

The following sections will deal with (1) the methods used to produce the CdTe absorber layers, (2) the methods used to produce the chalcopyrite compound absorber layers, (3) novel materials that have the potential to replace the more established materials, (4) the buffer layers, and (5) the TCO layers most commonly used and under development.

1.2 THIN FILM SOLAR CELLS BASED ON THE USE OF CdTe

1.2.1 HISTORICAL DEVELOPMENT OF CdTe SOLAR CELLS

The potential of using CdTe as an absorber-layer material in a solar cell has long been recognized. With a near-optimum, direct energy bandgap of 1.45 eV, CdTe-based solar cells can, in theory, be used to produce PV solar cell devices with efficiencies up to 27% [10]. Historically, CdTe homo-junction cells were the first to be investigated. However, the efficiencies were limited to <6% due to surface recombination. This arose because the high optical absorption coefficient of the CdTe meant that the collecting junction had to be located near the surface of the CdTe [11]. The first efficient polycrystalline thin film CdTe-based solar cell was the *p*-Cu₂Te/*n*-CdTe heterojunction solar cell. Such devices were also produced with conversion efficiencies up to 6% [12]. However, these solar cells were found to be unstable with the instability found to be associated with the use of the Cu₂Te layer.

In 1969, a *p*-CdTe/*n*-CdS heterojunction solar cell was fabricated with an efficiency of 1% [13]. This thin film solar cell device was made by evaporating CdS onto a TCO-coated glass substrate. CdTe was then deposited onto the CdS and then a metallic back contact onto the CdTe. Such a “superstrate configuration device” is shown in Figure 1.3. In 1972, an all thin film CdTe/CdS solar cell was produced by Bonnet and Rabenhorst with an efficiency >5% [14]. The promising efficiency and good stability of these devices stimulated worldwide interest in the development of CdS/CdTe thin film solar cells.

1.2.2 MATERIAL PROPERTIES

CdTe is part of the II^B-VI^A compounds family. With a direct energy bandgap of 1.45 eV and a large optical absorption coefficient (>10⁵ cm⁻¹) for the visible spectrum, only a few microns of CdTe are needed to absorb >95% of photons with energies >1.45 eV. CdTe is also amphoteric, i.e., it is possible to produce homojunctions with appropriate doping.

The temperature–composition phase diagram of CdTe has been described in detail by Zanio [11]. The melting point of CdTe is 1092°C which is significantly greater than Cd (324°C) and Te (450°C). This results in a large range of deposition temperatures available for the production of CdTe thin films. A detailed examination of the stoichiometric region reveals the presence of a symmetrical region which allows nonstoichiometric doping of the CdTe compound to be easily achieved. This makes the conductivity type of CdTe easily controllable. The crystal structure of CdTe is zinc

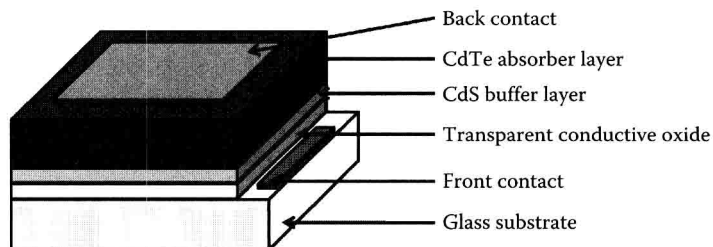


FIGURE 1.3 CdTe/CdS solar cell in superstrate configuration.

blende (Figure 1.4) with a unit cell length of 6.481 Å [15] and a CdTe bond length of 2.806 Å [16].

The most common defect levels in CdTe and their position relative to the conduction or valence band are shown in Table 1.3. Nonstoichiometric doping is achieved by controlling the concentration of native defects in the undoped material. Cadmium-rich growth enhances the formation of tellurium vacancies (V_{Te}), which can become positively charged. These defects act as donors, and the CdTe material grown is therefore *n*-type. The tellurium-rich film will be *p*-type, due to the presence of cadmium vacancies (V_{Cd} or V_{Cd}^{2-}), which tend to act as acceptor impurities. The CdTe and CdS layers can also be extrinsically doped in order to increase carrier concentration in each layer by adding appropriate donor or acceptor impurities. However, doping is usually achieved during a post-deposition heat treatment of the CdTe in air, following a dip in a solution of CdCl₂ in methanol or by the direct incorporation of CdCl₂ into the growing CdTe, followed by an anneal in air [11] (see Section 1.2.4.5 for further details).

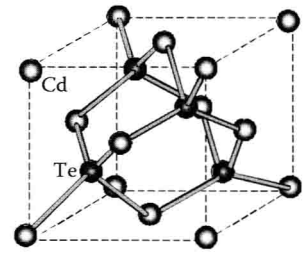


FIGURE 1.4 Unit cell of the CdTe zinc blende crystal structure.

1.2.3 DEPOSITION TECHNIQUES FOR CdTe

1.2.3.1 Thermal Evaporation

CdTe powder, or Cd or Te in the elemental form, can be heated to sublime onto an appropriate substrate, e.g., a glass slide. A schematic diagram of thermal evaporation is shown in Figure 1.5. Deposition is usually carried out in high vacuum, using a source temperature in the range 600°C–800°C and a substrate temperature in the range 100°C–400°C. A deposition rate of 1 μm/min can be obtained using a source temperature of 800°C and a substrate temperature of 100°C. Higher substrate temperatures result in a lower deposition rate. The as-deposited films often exhibit a [111] preferred orientation [24] and also a columnar grain structure [25]. The grain size strongly depends on film thickness and substrate temperature. Typically, for a 2 μm thick film, grain sizes range from 100 nm for a substrate temperature of 100°C to 1 μm when the substrate temperature is 350°C.

1.2.3.2 Sputtering

CdTe films can be successfully deposited by radio-frequency (RF) magnetron sputtering from compound targets. In the case of CdTe, the mass transfer of Cd and Te occurs via the bombardment of the CdTe target by Ar⁺ ions, followed by diffusion to the heated substrate (200°C–300°C) and

TABLE 1.3
Ionization Energy (eV) of Common Defects and Impurities in CdTe

Type	Acceptors						Donors				
	As_{Te}^-	$V_{Cd}Cl_{Te}^-$	V_{Cd}^-	V_{Cd}^-	V_{Cd}^{2-}	$V_{Cd}Te_{Cd}$	Cl_{Te}^+	V_{Te}^+	Cl_{Te}^+	V_{Te}^{2+}	Cd_i^{2+}
Ionization energy (eV)	0.10	0.12	0.14	0.45	0.60–0.74	0.74	0.014	0.04	0.07	0.40	0.64

Sources: Hoschl, P. et al., *Mater. Sci. Eng. B*, 16, 215, 1993; Abulfotuh, F.A. et al., Study of the defects levels, electrooptics and interface properties of polycrystalline CdTe and CdS thin films and their junction, in *Proceedings of the 26th IEEE Photovoltaic Specialists Conference*, Anaheim, CA, 1997, p. 451; Emanuelsson, P. et al., *Phys. Rev. B*, 47, 15578, 1993; Wienecke, M. et al., *Semicond. Sci. Technol.*, 8, 299, 1993; Krsmanovic, N. et al., *Phys. Rev. B*, 62, 16279, 2000; Berding, M.A., *Phys. Rev. B*, 60, 8943, 1999; Capper, P. (ed.), *Properties of Narrow Gap Cadmium-Based Compounds*, INSPEC, London, U.K., 1994.

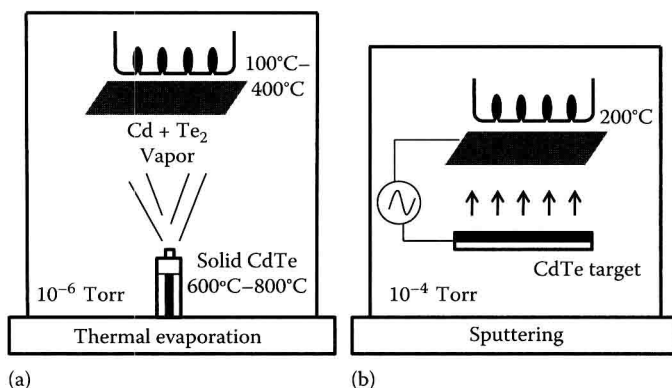


FIGURE 1.5 Schematic diagrams of thermal evaporation (a) and sputtering (b) deposition techniques.

condensation. A schematic of a simple sputtering system is shown in Figure 1.5. The typical deposition rate is 100 nm/min. As-deposited films (2 μm thick) have a grain size of ~ 300 nm with nearly random grain orientation [26].

1.2.3.3 Close-Spaced Sublimation

Close-spaced sublimation (CSS) is a widely used technique for depositing CdTe and is in fact a modified version of the thermal evaporation method. To date, the most efficient cells use CSS-deposited CdTe [27–30]. This technique is based on reversible dissociation of CdTe at high temperature. The source material is maintained at a higher temperature (e.g., 650°C) than the substrate (e.g., 550°C), a few mm away from it (Figure 1.6). The source dissociates into its elements that recombine on the substrate surface. The deposition occurs through a flowing gas that can be N₂, Ar, He, or O₂. This deposition technique is characterized by a high deposition rate (>1 $\mu\text{m}/\text{min}$), a nearly random orientation of the as-deposited film [24], and a large grain size (several μm) [31].

1.2.3.4 Vapor Transport Deposition

Vapor transport deposition (VTD) is a high-rate deposition technique, also sometimes referred to as modified CSS. This technique was developed by Solar Cells, Inc. [32,33], and deposition occurs by the transfer of Cd and Te vapors from heated CdTe onto a moving and heated substrate

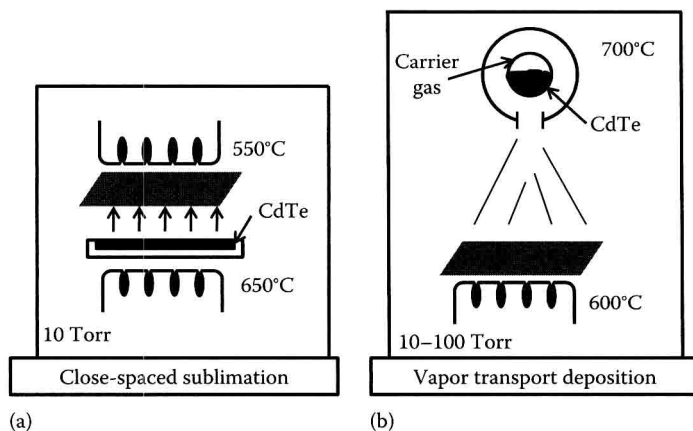


FIGURE 1.6 Schematic diagrams of CSS (a) and VTD (b) deposition techniques.