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Technological Background and Properties of Thin Film Semiconductors

Orkut Sancakoglu

Abstract

Especially with the development of nanotechnology and polymer science, interest in research and production of both efficient and lower-cost semiconductor thin film materials is increasing day by day. The use of nano-structured thin films for efficient use of solar cells in production of n-type semiconductor materials is one of the most important sources of energy and new-generation energy. Considering the indicated trends and energy requirements, it has been important to transfer this technology in detail regarding the surface technologies related to the semiconductor materials produced with thin film technologies instead of bulk materials. With this aim, this book chapter “Technological Background and Properties of Thin Film Semiconductors” includes a brief story about semiconductors, band gap theory, thin film applications, and besides traditional thin film processing methods finally a new technology called aerosol deposition technique which allows room temperature processing of several materials for semiconductor applications, respectively. It is thought that it will make important contributions to the relevant field and bring a new perspective and direct scientific research in “process-structure–property–performance” relation.

Keywords: thin film semiconductors, transparent conducting oxide (TCO), coating, room temperature aerosol deposition, transparency, resistivity

1. Introduction

Semiconductor materials are defined as materials in solid form whose conductivity has a value between conductors and insulators. Semiconductor materials play an important role in the advances in the modern electronics industry in the twenty-first century and in the industrial applications of many electronic devices. These materials include many materials such as silicon, gallium arsenide, germanium, cadmium sulfide, and cadmium telluride, which are widely used today. From the first silicon integrated circuits produced in semiconductor technology, high-tech microprocessors, solar cells, and many other electronic devices have developed rapidly to the present day [1].

Especially with the development of nanotechnology and polymer science, interest in the research and production of both efficient and lower-cost semiconductor thin film materials is increasing day by day. The use of nano-structured thin films for the efficient use of solar cells in the production of n-type semiconductor

materials is one of the most important sources of energy and new-generation energy. In short, semiconductor devices for nanotechnology and polymer science have taken the advancement of research in semiconductors to a new step, aiming to improve the chemical and physical properties of these materials. To understand the nature of these crucial engineering materials, the difference and theory between conductors, insulators, and semiconductors must be fully understood. In addition, basic concepts such as band theory, doping processes, and p-n junction theory of solids are theoretical bases that will give a general idea of understanding semiconductors.

2. Technical background

It is important to assimilate the band theory that explains the nature of semiconductors in terms of energy levels between the valence and the conduction bands in order to gain knowledge about semiconductor materials. The main difference between metallic materials and semiconductors is that the current is provided by electron flow in metallic conductors, whereas in semiconductors this flow occurs not only by the electron flow but also by the flow of positively charged holes.

Electrical conductivity is directly related to the band structure of a material. If we look at the basis of the theory, atomic energy levels of each atom are equal when two different atoms are sufficiently distant from each other. However, as these atoms approach each other, differences in the original energy levels of the atoms are observed, and as a result of these differences, an interaction occurs that creates molecular bands between the atoms. Therefore, it is for this reason that materials with different band structures show different conductivity properties. In conductors, the energy difference between partially filled energy levels and empty levels is very low. Therefore, when a potential is applied to metals, electron mobility between the filled and empty levels, which takes place by using very low energy, is easily realized, and the flow of electrons is provided. Therefore, it would not be the right approach to talk about an obstacle between the levels defined as valence band and conduction band in metals. As known, an electron must have an empty energy level to move, otherwise electrons cannot move in solid material. Based on this approach, it can be clearly understood why electrical current is not observed in insulating structures. In insulators, the valence band is the highest band fully filled by electrons, and the conduction band is the lowest empty band, with a forbidden band gap of about 5–10 eV between these two bands [2]. This broadband between the valence band and the conduction band prevents the transmission of electrons to the conduction band, and no electrical current is generated in the insulating materials. Similar to the band structure of the insulators, semiconductors have a valence band occupied by electrons and a conduction band ready to be filled with electrons. In semiconductors, just like insulating materials, there is a band gap between these two bands. The main difference between the band gap in these two groups excluding conductors is that the band gap value is much smaller in semiconductors (1.1 eV for silicon) than in the insulator [3]. Since the thermal energy in semiconductors creates the driving force for the movement of electrons, the conductivity of these materials is directly related to the temperature. The conductivity of a semiconductor material as a result of a decrease in resistivity can be associated with increased kinetic energy with temperature. **Figure 1** schematically shows the energy band gaps in conductors, semiconductors, and insulators.

In semiconductors, the valence band that is below the forbidden band gap is almost completely full. On the other hand, there is a nearly empty conduction band over the prohibited band gap. When a semiconductor material is excited, if the

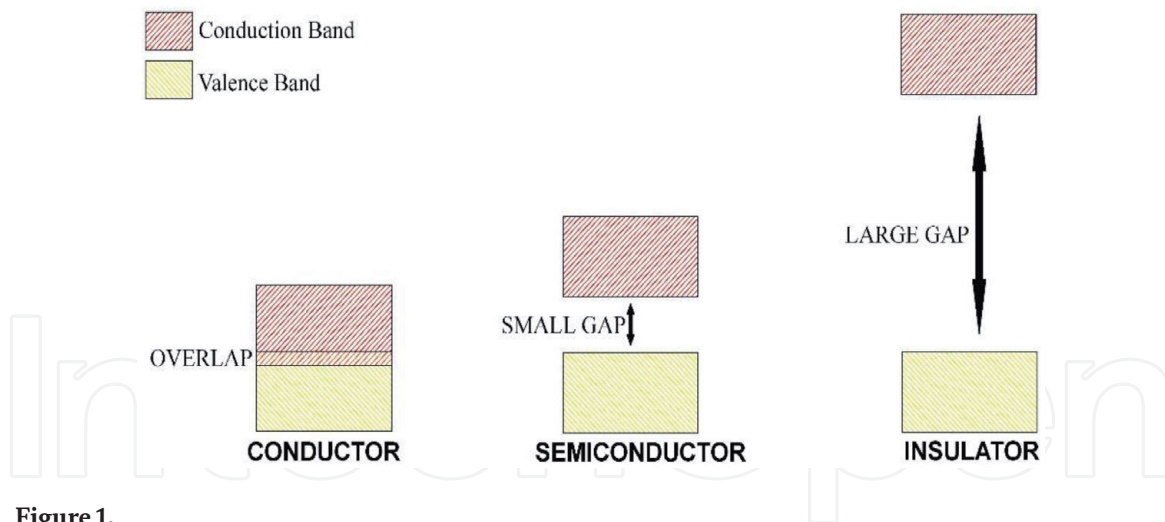


Figure 1.
Energy band gaps in materials.

energy of the photon is greater than the band gap, the electrons will easily pass to the conduction band, and electrical current will occur. According to the theory, as a result of the transition of an electron to the conduction band, the excited electron leaves a hole in place that can flow through the material and act as a positively charged particle. Here, carrier production and recombination can be defined as two basic factors in the creation of charge-carrying electrons and positively charged holes [4].

3. Types of semiconductors

In general, depending on the level of doping, semiconductors can be classified into two main groups such as *intrinsic semiconductors* and *extrinsic semiconductors*. The intrinsic semiconductors are pure semiconductors and no addition is made. In this type of semiconductor, conductivity is provided by the thermal stimulation of electrons. At the same time, the number of excited electrons and positively charged holes is equal. The behavior here appears as a result of the carrier production and recombination steps [5].

On the other hand, extrinsic semiconductors have low conductivity values, and an important process called *doping* is applied to overcome the problems encountered in applications and to increase the conductivity [6]. This process can be explained simply by adding small amounts of impurities in the concentrations of charge-carrying electrons and positively charged holes, thereby increasing the conductivity level. The aim is to change the electronic structure by impurity addition into the structure without changing the crystal structure. For example, arsenic with five valence electrons to an atom and germanium with four valence electrons will cause the arsenic atom to covalently bond with the germanium atom. The extra fifth electron of the arsenic atom will have the electrical conductivity as it will have the freedom to move from one atom to another [4]. Such semiconductors, which the dopant element donates an electron, are called n-type semiconductors. In addition to producing free electrons in n-type doping, an equal number of positive charges are also produced in pairs with free electrons. As a result, the doped semiconductor material remains electrically neutral. However, these positive charges should not be understood as positively charged holes. These charges occur in the absence of free electrons, but do not contribute to a current flow. Another contribution of free electrons to pure semiconductors is that the donor electron is much closer to the conduction band than an electron in the valence band of the original atom.

In another saying, the energy level of the donor electron is at another level that is much narrower than the energy level for valence electrons and facilitates the flow of current in the n-type semiconductor.

In another type of extrinsic semiconductor, if a pure semiconductor with trivalent electrons (e.g., germanium) is replaced by gallium, this type of semiconductor is called p-type semiconductors. Three of the four covalent bonds are occupied in the structure; the bond remains empty and acts as a relatively moving hole in the opposite direction of a moving electron, which is not a real move. The main phenomenon is defined as a relative movement caused by the movement of electrons from one bond to another and leaving a hole after. Similar to the energy band structure of n-type semiconductors, which differs from pure semiconductors, p-type semiconductors also have a higher acceptor energy level than the valence band.

4. Application fields and thin film technology

Materials are produced with developing semiconductor technology; it has been used for more than 50 years in the production of a wide variety of devices such as diodes, transistors, sensors, microprocessors, and solar cells. On the other hand, thin film nano- or microstructures are frequently used in applications developed in semiconductor technology. The most common area that benefits semiconductor thin film technology refers to photovoltaic applications. Simply, this application is the technology field for using solar cells to produce solar energy. The importance of photovoltaics comes from the fact that photovoltaics are not only important in terrestrial applications to gain renewable and clean energy but also enable the benefits of solar energy which can be used as a major source of electrical power for space systems [7]. Besides, all the concerns based on environment, renewability, and sustainability have increased attention for using alternative, new energy sources, where photovoltaics are seen as the new trend.

In general, semiconductor thin films are produced in one or more thin layers. Common applications of such structures include many electronic materials such as transistors, sensors, and photovoltaic devices. The structural, chemical, and physical properties of semiconductor thin films are directly related to the production technique, and their thickness ranges from a few nanometers to hundreds of micrometers [8].

Especially in recent years, semiconductor thin films can be obtained compared to the use of bulk materials, making it a promising ideal candidate in the electronic material industry due to its wide variety of properties. First of all, a wide range of chemical, electrochemical, and physical deposition techniques (see Section 5) enables the low-cost production of semiconductor material on large areas of the desired geometry and structure. In addition, single- or multi-crystalline structures with complex geometry and even microstructures of nanocrystalline thin films can be easily obtained by changing the method, temperature, substrate, and other production parameters depending on the method. Industrial applications of electronic materials come to life with different junction types between different semiconductor materials to improve the electrical properties of thin films.

Thin film solar cells, which we have already mentioned and attracted great interest from researchers, consist of materials of different structure and properties in the form of several thin layers deposited on various substrates. To draw a general schematic, the common structure of a solar cell consists of a hard or flexible substrate, a transparent conductive oxide (TCO) layer, a window layer made of n-type semiconductor, p-type semiconductor layer, and a metal contact and absorbent

layer. In order to make the structure more understandable, the schematic of a solar panel is examined in **Figure 2** [9].

Additionally, the flowchart of solar energy diagram using the panels is given below sequentially:

- i. Solar panels convert sunlight to DC current.
- ii. Inverter converts DC electricity to AC.
- iii. Electricity then gets used by home applications.
- iv. Extra electricity gets credited into the grid.

In a solar panel, each of the components given in **Figure 2** has different physical and chemical properties. The performance of the solar cell depends on the properties of the previously mentioned layer components and the compatibility between them. The layers described should be mechanically and chemically stable as well as compatible with each other based on their properties. The high processing temperature, which is a requirement of most processes, results in the need of a hard substrate such as glass, because flexible substrates (can be polymeric, etc.) do not have high temperature stability. On the other hand, it is reported that the choice of the substrate has a direct effect on the efficiency of the cells and the grain structure of the films grown on this substrate [10–12].

When it comes to the transparent conductive oxides, which are among the trend research subjects of recent years (see Section 6), it provides an integration between the substrate and the window layer with good electrical conductivity and high optical permeability in the visible region. In order to reduce the total resistance of the system, high transparency is required for good conductivity feature and higher degree of light passing through the absorbent layer. The window layer, on the other hand, has the function of directing the maximum amount of incoming light to the junction point and the absorbent layer in a hetero combination with an absorbent

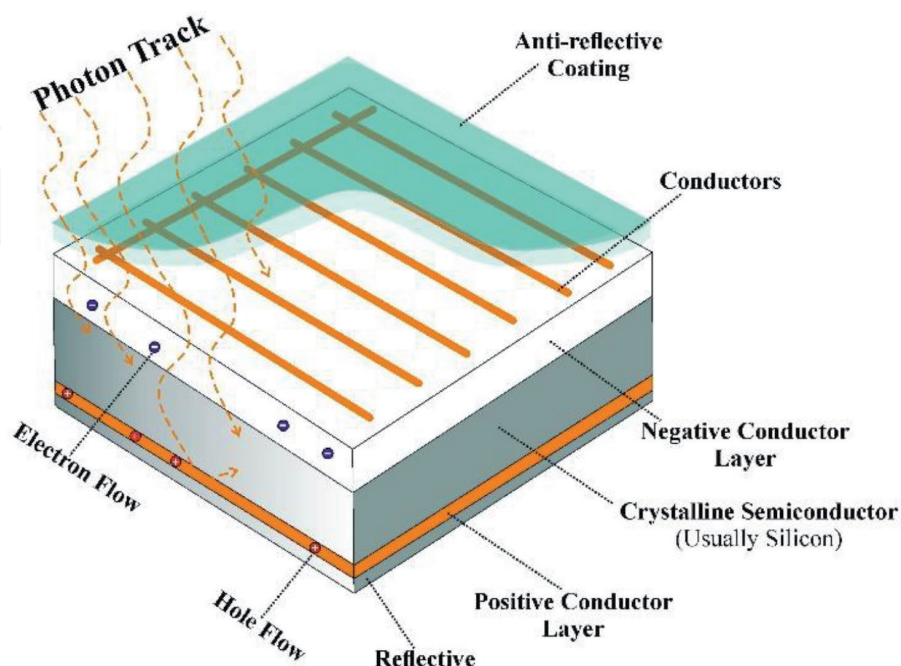


Figure 2.
Schematic of a laminated solar panel.

layer. Moreover, the compatibility of the window layer with the absorbent layer and the lattice structure is of great importance for device performance.

5. Thin film processing

The coating process is the basis for the production of devices based on thin film technology. In improving device performance, high-quality thin films produced by using rapid, economical, and effective techniques are required. The semiconductor industry, which is almost entirely based on solid thin films, has demonstrated the importance of coating technology and has contributed to its rapid development, especially in recent years. In this context, there are various methods for creating thin films on nano-micro scale. Basically, deposition techniques can be divided into two groups as chemical and physical methods [13].

Subgroups of chemical and physical deposition methods can be defined as (i) chemical vapor deposition (CVD), including chemical bath deposition, electroplating, molecular beam epitaxy, and thermal oxidation, and (ii) physical vapor deposition (PVD), including evaporation and spraying. It is possible to mention that CVD and PVD have an important place in new-generation thin film technologies.

Of these techniques, CVD is used to create high-purity and effective solid thin films [14, 15]. In this process, the substrate is placed inside a reactor where it is exposed to volatile gasses, and a solid layer is formed on the substrate surface by chemical reactions between the gas used and the substrate. CVD method can produce high-purity single- or polycrystalline or even amorphous thin films. Another feature of CVD is that both pure and complex materials can be synthesized at the desired purity at low temperatures. The chemical and physical properties of the forms to be created can be easily adjusted by properly adjusting the reaction and precipitation parameters such as temperature, pressure, gas flow rate, and gas concentration.

As another technique, PVD can be defined as thin film production by condensing the evaporated materials released from a source (target material) on the substrate surface. Sub-methods of this technique are spraying and evaporation, respectively.

Spraying method is based on the principle of removing surface atoms from a target and depositing them on the substrate. Among the advantages of the spraying method, thin films with the desired composition closest to the composition of the target material can be easily obtained. Besides, the method provides better adhesion to the surface, and evaporation of materials with a high melting point is possible.

Evaporation is another common PVD method in thin film production. In this technique, the evaporated particles are condensed on the substrate to form a solid thin film, while the source material (mostly metallic) is evaporated in a vacuum tube. The great advantage of evaporation compared to sputtering is that the process is relatively faster.

6. Future technology based on TCO semiconductors

Due to the wide range of applications mentioned in Section 4 and the unique optical and electrical properties that can be combined, TCO materials are used in transparent and flexible device applications such as flat panel displays, plasma screen panels, organic light-emitting diodes, solar cells, and gas sensors. As the most common TCOs, indium, tin, cadmium, and group III and VII doped zinc oxide can be mentioned. It consists of semiconductor metal oxides with a wide band gap.

These materials show high conductivity, transparency, and reproducibility, and the possibility of producing very flat films and tin-doped indium oxide (ITO) is the most employed TCO. Due to the cost and difficulty of finding indium in TCO, cost-effective and alternative materials with the same properties are needed. In addition to high conductivity TCO, the development of materials other than ITO has increased in few years. ITO's cost and potential supply limit are among the reasons for research in this field. Current candidate materials for high conductivity TCOs include CdO, SnO, In₂O₃, and ZnO with these binary combinations along with alternative additives. ZnO as the current candidate is considered to be the primary candidate of binary oxide TCO materials, with its high conductivity and low cost. However, it is very sensitive to oxygen, and process control is more difficult; the development of ZnO with alternative impurity continues.

ZnO:Al (AZO) produced with pulsed laser deposition (PLD) shows at least equivalent resistivity with ITO. However, PLD is not considered to be a suitable deposition method for large area applications. Metallic and ceramic targets are used to develop robust process control and to scale wide area bases in the production magnetron sputtered (MS) ZnO:Al (AZO) films. AZO and ZnO:Ga (GZO) are both commercially applicable in thin film solar cells and can be used as translucent electrodes [16].

In ZnO film growth, several techniques with their own advantages and disadvantages are used such as evaporation, radio-frequency magnetron sputtering (RF-MS), direct current magnetron sputtering (DC-MS), ion beam sputter, spray pyrolysis, sol-gel process, PLD, and CVD. Transparent n-type ZnO semiconductors can easily be fabricated by B, Al, In, and F doping. According to the results of several research in which RF-MS, DC-MS, and MOCVD are used, ZnO:Al with relatively low resistivity values is found to be 1.4×10^{-4} , 3.4×10^{-4} , and 3.0×10^{-4} Ωcm , respectively. These resistivity values are quite close to the electrical properties of ITO. The optoelectronic properties of these thin film TCOs may change after thermal annealing in an inert gas or reactive gas atmosphere [17].

Lastly, if we consider PVD as one of the trending methods in the past few years and even a more innovative sub-method, the magnetron sputtering technique, the applicability problems brought by the researcher who has practical experience in this field and the applicability of the method to large surfaces as an assessment of the literature-scale results are known. In such semiconductor materials, homogeneity is another problem to be solved and mostly at high-temperature processes after coating (additional heat treatments). This makes the aforementioned method disadvantageous. In addition, while many traditional methods used in semiconductor technologies are generally suitable for coating applications on metal or ceramic substrate, the phase transformation and/or defect removal with additional heat treatments makes these techniques unsuitable for developing polymer-based semiconductor applications for high-technology semiconductor field.

From this point of view, the search for alternative methods that will meet the advancing technology and meet technological requirements not only for metal and ceramic substrates but also polymer-based ones encouraged researchers to work on new techniques and methods. "Ceramic powder aerosol deposition method," which is pointed, is not only requiring additional high-temperature heat treatment or sintering steps but also homogeneous and continuous applicability to large areas. It has become a trend that draws the attention of researchers on semiconductor material technologies annually. As a result of all these advantages, the aerosol deposition method has been deemed worthy of examination both in terms of its technical details and applicability, and because it is a virgin technology that is still open to development in the field, it may meet the need in new-generation semiconductor technologies.

Aerosol deposition technique, in terms of homogeneous, continuous, and applicability to large area TCO, is a convenient method for industrial production of materials that has not been studied much before. As it is known, new-generation ceramic integration technologies require device performance improvement for various applications such as size reduction and/or micro-mechanical systems, image technologies, fuel cells, and optical devices. Common industrial applications of these devices are high-speed coatings and productions that bring low processing temperatures and thin lithographic processes in ceramic coatings. “Ceramic powder aerosol deposition method” has many advantages to meet many of the requirements mentioned above when compared to other conventional film/coating applications.

While ceramic material productions generally require sintering over 1000°C , this makes it impossible to integrate metal, glass, and even polymers with relatively low melting point with functional ceramics. On the other hand, high-temperature film applications trigger high-temperature crack formations and substrate-coating incompatibilities and discontinuities, as well as long processing times. Especially in film-type applications, the substrate-coating incompatibilities and surface discontinuities will adversely affect the optical, electrical, and mechanical properties of the device for the application and also decrease its performance. Similar results were observed in our previous research studies in the form of surface cracks and unexpected decrease in electrical properties as a result of ZnO-based coatings obtained by magnetron scattering method, which requires additional heat treatment up to 700°C .

The main output of the aerosol deposition method in the development of a new technique and industrial product with high-speed coating efficiency, low processing temperature, and even at room temperature reduces costs and production time and adversely affects properties.

The basic principle of the technique is based on the conversion of some of the kinetic energy of the previously prepared and suitable form of fine ceramic particles with the substrate at high speeds, into both interparticle and interparticle-binding energy. In this context, while the aerosol deposition method offers many advantages compared to traditional thin/thick film methods and thermal spray coating techniques, it has not been fully understood as a new method, revealing the open points for the research. A schematic of this method is given in **Figure 3**.

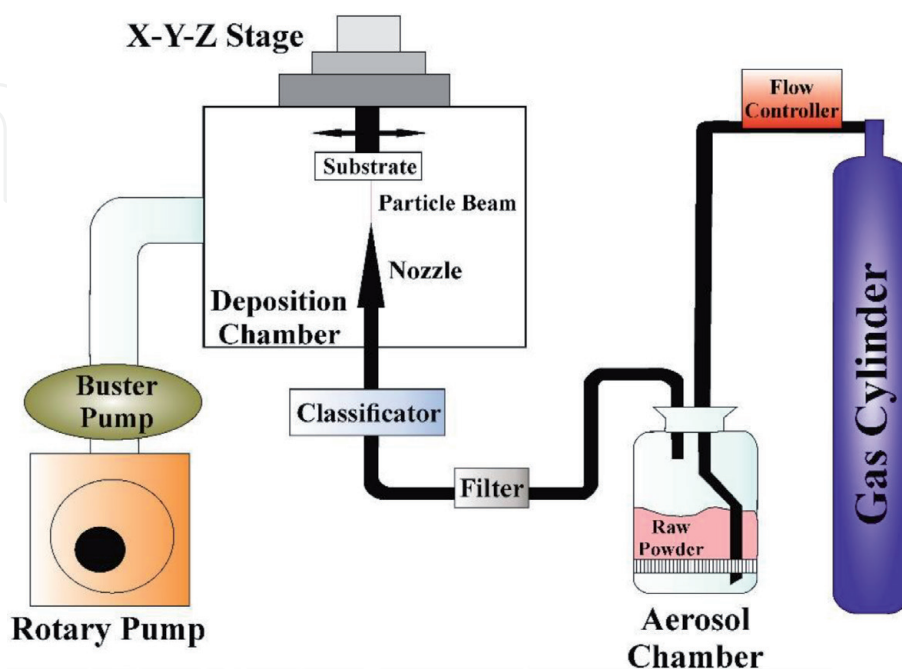


Figure 3.
Room temperature aerosol deposition system.

Simply, aerosol deposition method is based on the principle of ultra-pressure ceramic particles coming together with the surface of the substrate and solidification with effective pressure and shock loading. First, ceramic particles are mixed with a gas in the system chamber to form an aerosol. This aerosol is then sprayed through a nozzle onto various targets to create a film layer with the aid of pressure. During the process, some of the kinetic energy of the particles is converted into thermal energy, which partially increases the temperature in the interaction zone. In this way, the bonding between the substrate and the particles and also the particles with each other is provided and results in a high-density continuous coating layer.

In general terms, aerosol deposition technique is as follows:

- Appearing as a suitable method for all types of substrates.
- As a horizon for the electronics industry.
- Not only for energy conversion applications but also for various semiconductor technology applications.
- Does not require additional heat treatment.
- Most importantly, as it is a low-temperature process, in terms of being a feasible method without changing or destroying the substrate form.

It is thought that this new technology will make important contributions to the relevant field and bring a new perspective and direct scientific research in process-structure-property-performance relation.

7. Conclusions

Due to the cost and difficulty of finding indium in TCO, cost-effective and alternative materials with the same properties are needed. In addition to high conductivity TCO, the development of materials other than ITO has increased in few years. ITO's cost and potential supply limit are among the reasons for research in this field.

Besides, not only for the metallic and/or ceramic substrates but also for the substrates with low melting point or polymers need to be focused on new semiconductor fabrication technologies. At this point, room temperature aerosol deposition method seems to be an alternative technique and may bring a new perspective in high-technology semiconductor applications.

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