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Metal oxide thin film transistor and its active layer materials

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Abstract. Metal oxide thin-film transistors (MOTFTs) have the characteristics of high electron mobility, large-area production, and relatively low fabrication temperature and have received extensive attention as a research hotspot in recent years. Based on a large number of literatures, this paper introduces the typical single-component representative of MOTFT, multi-component compound oxide semiconductor active layer materials such as IZO, IGO, IGZO, etc. At the same time, due to the unique advantages of nanomaterials, material modification is carried out in different dimensions, and six physical and chemical preparation methods of its active layer are described, including a relatively unique Low-temperature preparation method based on improved gel precursor components and UV photocatalysis. Multi-component oxides and composite structures based on nanomaterials are currently the most studied fields, and on this basis, more excellent performance can be studied and prepared. It mainly summarizes its application in large-scale display and flexible electronics and looks at its development direction.

Keywords: Thin Film Transistor, Metal Oxide, Active Layer, Semiconductor.

1. Introduction

A thin Film Transistor (TFT) is a field-effect electronic component composed of a flexible substrate, a gate electrode, a source-drain electrode, a dielectric layer, and an active layer [1-3]. The source and drain methods can be divided into top-contact and bottom-contact methods, and the gate position can be divided into top-gate and bottom-gate structures. TFTs are usually divided into four structures: bottom gate bottom contact, bottom gate top contact, top gate bottom contact, and top gate top contact, as shown in Figure 1 [4].

The active layer semiconductor material is the main factor determining TFTs' transport characteristics. In recent years, metal oxide thin film transistors (MOTFTs) using metal oxides as active layer materials have received extensive attention as a research hotspot. Metal oxides belong to the third generation of semiconductors. They have high exciton binding energy, largely forbidden bandwidth, small dielectric constant, and other characteristics of the fabricated transistor have high electron mobility [5, 6], which can be applied to various products such as e-books, liquid crystal displays, and TV screens

[7]. As a more high-end avant-garde material, scientists are bound to take advantage of it and let it shine in the field.

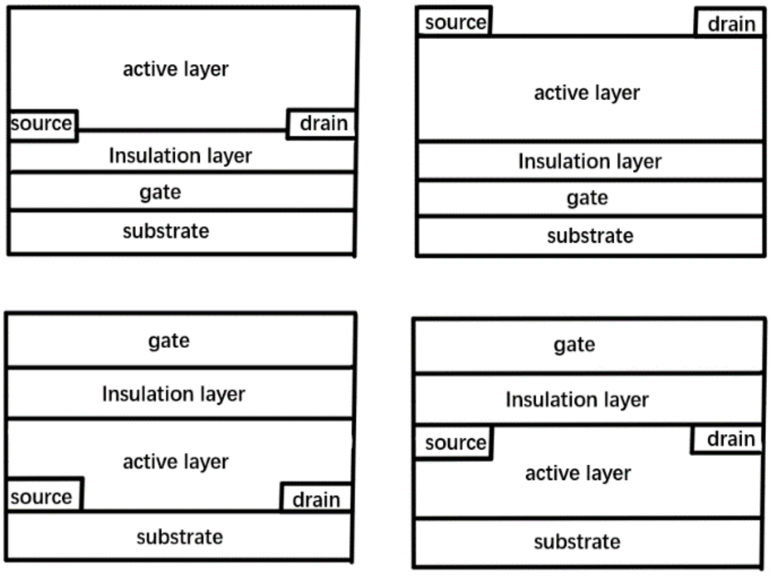

Figure 1. Four basic structures of TFT.

In 2003, Hoffman et al. first prepared a TFT based on a ZnO semiconductor active layer with electron mobility of 0.3~2.5 $cm^2/(V \cdot s)$ [8]. in 2004, Nomura's group first prepared a TFT based on an IGZO semiconductor active layer. , the electrical mobility is as high as 80 $cm^2/(V \cdot s)$ [9]. In 2005, DuPont Printing Company first reported black and white electronic paper based on oxide thin film transistors; in 2010, SMD Corporation combined TFT and polyimide substrates based on IGZO semiconductor active layers to develop a 6.5-inch color flexible display [10]. In 2022, LG will exhibit a 55-inch transparent display based on MOTFT at CES [11]. It can be seen that the performance of MOTFT has been continuously improved in the past ten years, and the product application has been gradually realized, which has great development potential.

Based on a large number of literatures, this paper focuses on the active layer semiconductor materials and preparation methods of MOTFT, summarizes the application of MOTFT in its advantageous fields, and makes an outlook on its development direction.

2. Oxide semiconductor material

The performance of MOTFT is mainly affected by the field effect mobility of the device. Mobility refers to the average drift speed of carriers (electrons or holes) under the action of a unit electric field, and the selection of the active layer oxide semiconductor material directly determines the level of mobility. Currently, single-component and multi-component oxide materials have been deeply studied and widely used in the preparation of MOTFT, and the emerging compound oxide semiconductors provide a new research approach for developing high-performance MOTFT.

2.1. Single component oxide

The single-component oxides are mainly ZnO, SnO, In_2O_3, Ga_2O_3. Different components have different crystal structures, which mainly affect the field effect mobility of the device [12]. However, they generally have a large band gap and high conductivity. ZnO has a hexagonal wurtzite structure, In_2O_3 has a cubic symmetric bixbyite structure, SnO_2 has a rutile structure, and Ga_2O_3 has a variety of complex crystal structures, specifically.

Although the crystal structures are different, their metal cations have the special electronic structure of $(n-1)d^{10}ns^0$. The overlapping of these spherical orbitals can produce a wide energy band distribution,

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which provides good conditions for electron transport so that it generally has a large band gap, electrical conductivity, and high mobility, exhibiting excellent semiconductor properties [13, 14]. However, the single-component oxide preparation of TFT is prone to the problem of grain boundary defects, which makes the obtained device structure non-uniform and unstable in electrical properties. It is necessary to improve the applicability of doping and other means.

2.2. Multi-component oxides

Multi-component oxides are mainly In-Zn-O (IZO), In-Ga-O (IGO), Zn-Sn-O (ZTO), and In-Ga-ZnO (IGZO), and they have different lattice structures. Amorphous materials can be obtained by mixing component materials. Compared with single-component oxidation, which is prone to defects. It has better uniformity and excellent electrical stability and has higher carrier concentration. Also, it can be used in thin film transistors to obtain excellent mobility properties [15]. IZO has a unique superlattice structure and zig-zag modulation structure. It has electrical anisotropy and excellent properties such as high mobility and threshold voltage. However, due to the easy formation of oxygen vacancy defects, the free electron density is high, and the film is stable. The performance of IZO-TFT can be improved by the alkaline earth metal co-doping method (Ba and Sr)/sputter deposition of the ATO gate insulating layer [16]. IGO also faces the problem of poor stability, like most MOTFTs, although IGO is attractive. Therefore, Zhu's group incorporates the rare earth element Pr into the IGO material to help reduce the defects of oxygen vacancy formation [17]. The chemical properties of ZTO are relatively stable; the band gap of the film is 3.6 eV, and it has high light transmittance. It can realize the transformation of crystalline and amorphous states through preparation methods and has high chemical sensitivity. ZTO is mainly made of Zn and Sn, abundant on earth, so ZTO has good development prospects.

IGZO has excellent electrical properties and low production cost, which has a high degree of commercialization and occupies a major market share. However, the relatively weakly bound Zn-O bonds are prone to breakage and form defects that affect device performance. The current research focuses mainly on the ratio of In/Ga/Zn, the active layer's growth temperature, the active layer, and the thickness of the active layer [18]. For the In/Ga/Zn ratio, the Zn content affects the stability of IGZO-TFTs, and the In and Ga contents change the carrier concentration by affecting the number of oxygen vacancies, affecting the performance of IGZO films. For the growth temperature of the active layer, SUN does not need to undergo thermal annealing treatment by doping Al_2O_3 as the active layer, and the finished product exhibits excellent on-off ratio and bias stability finally [19]. ZHU uses it to explore the effect of temperature on organisms' influence [20]. For the thickness of the active layer, Kumar's analysis verifies the variation of film physical properties and oxygen vacancies with the thickness of IGZO [21]. In addition, Zhang et al. completed the direct writing preparation by engraving on the surface of any shape through the micro-pen direct writing technology, which is convenient for expanding the application environment further.

2.3. Complex oxide

With the boom of nanomaterials, TFTs based on nanoparticles of different dimensions have also been developed. The effective length of the conductive channel of the top-gate structure and the energy barrier of the electron transport process is reduced by the communication layer of the nanodot composite IGZO TFTs so that the device has a high mobility of 79 $cm^2/(V \cdot s)$.

In the field of one-dimensional nanomaterials, the fabrication of TFTs represented by indium oxide nanowires has attracted attention due to their excellent electrical and optical properties, effectively regulating the threshold voltage [22]. At the same time, SWNTs have high electrical conductivity, excellent mobility, and flexibility. The application of SWCNTs based on IZO to fabricate p-type TFT devices has good electrical properties under a certain operating voltage.

In the field of two-dimensional nanomaterials, graphene provides the ultimate choice for thin 'channel' transistors. The preparation method of graphene can control its mobility and has gained new opportunities for circuits that rely on nonlinear responses because of its bipolar nature [23]. Graphene-based semiconductor devices can achieve high sensing and low-noise properties; especially bipolarity

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provides a new way to address the study of solid or liquid interfaces. In addition to graphene, cellulose grids are also a new option. Nanocellulose has good flexibility and controllable pore size, especially for ITO transistors that use it as a gate dielectric. At this time, the multi-gate structure of the new structure device has more excellent circuit logic functions.

3. Preparation of active layer in MOTFT

The essence of the active layer's preparation in MOTFT is synthesizing metal oxide thin films. The preparation methods are mainly divided into physical and chemical methods. The former include magnetron sputtering, pulsed laser deposition, and molecular beam epitaxy. The latter include spin coating, spray coating, and low-temperature solution processing [4, 24, 25, 26]. The applicable materials and the properties of the films produced by distinct methods are different, and the application fields are also variant.

3.1. Magnetron sputtering

Magnetron sputtering belongs to vacuum film coating, and the basic principle is as follows: After the sputtering chamber reaches the required vacuum degree and a strong electric field is formed between the substrate and the sputtering target, high-speed energic electrons collide with the Argon molecules to ionized into argon ions and secondary electrons. Then, argon ions hit the target surface and sputter out the target atoms, while secondary electrons participate in the next impact and cause ionization, as shown in Figure 2 [4, 14, 27-29].

Thin film prepared by magnetron sputtering has the advantages of uniform thickness, good stability, and high substrate adhesion. At the same time, this type of thin film has high repeatability because the formation speed of the film can be controlled by adjusting the electric field intensity, and the thickness of the film can be controlled by adjusting the sputtering time, which means that it can be widely used in laboratory research and industrial production.

The disadvantage of magnetron sputtering is that the vacuum degree required for the sputtering chamber makes related equipment costs high, and the vacuum environment limits the area of the film that can be prepared to a certain extent. Currently, most MOTFT can be prepared by magnetron sputtering, and ITO film has achieved mature industrial production by magnetron sputtering [7].

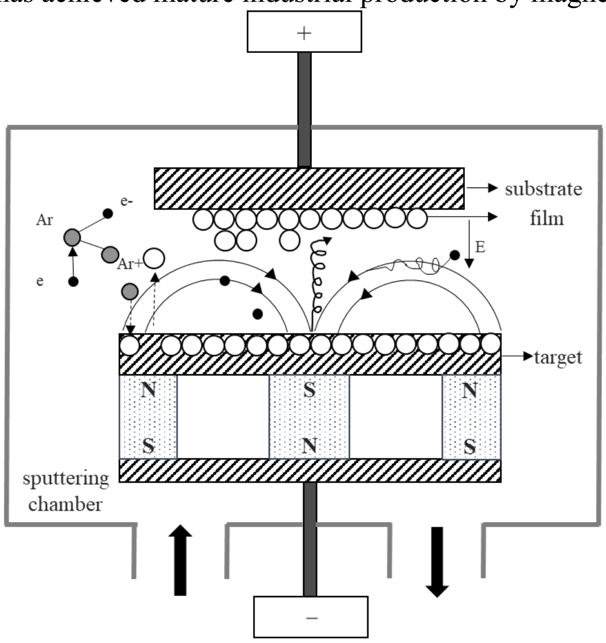

Figure 2. The principle of magnetron sputtering.

3.2. Laser pulse deposition

Laser pulse deposition (LPD) belongs to vacuum evaporation coating, and the basic principle is as follows: Irradiating the target surface with high energy laser to form a plasma, and after directional isothermal adiabatic expansion, the plasma is emitted to the outside and deposited on the substrate surface to form thin films, as shown in Figure 3 [4, 28, 30].

The advantage of LPD is epitaxial film formation because the epitaxial film's growth rate, growth temperature, and stoichiometric ratio can be precisely controlled. The disadvantages of LPD are that the equipment cost is too high, and the uniformity of large-size film preparation cannot be guaranteed. Currently, LPD is limited to laboratory research and use, and it is not easy to further industrialization. LPD is mainly used to study and prepare ZnO thin and composite films [13].

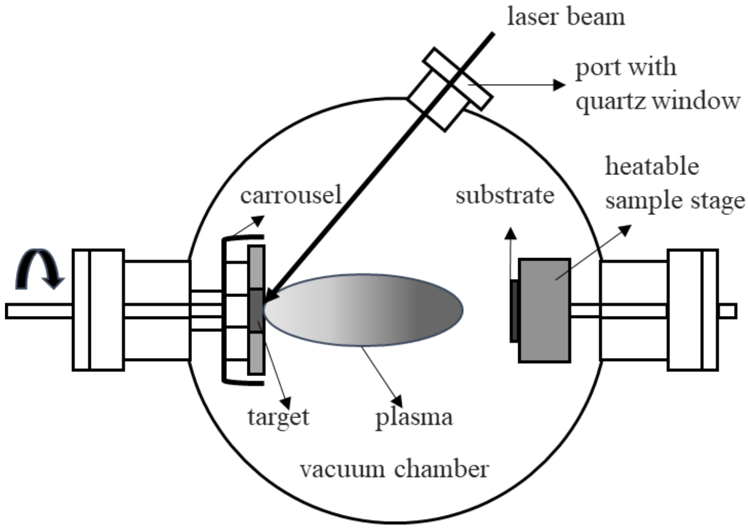

Figure 3. The principle of laser pulse deposition.

3.3. Molecular beam epitaxy

Like laser pulse deposition, molecular beam epitaxy (MBE) also belongs to vacuum coating. The basic principle is that molecular beams can be generated from raw materials through high-temperature evaporation, electron beam heating, gas splitting, and other methods in an ultrahigh vacuum chamber. Then, the molecular beams are sprayed onto the substrate and epitaxially grow into a film after nucleating, as shown in Figure 4.

MBE can accurately control the chemical composition and doping concentration of the film. Meanwhile, the film forming rate is so low that it can realize the growth of single crystal film and control the thickness of the film, which means MBE is suitable for preparing high-performance active layer film. MBE has been maturely used in experimental research, but its industrialization is limited by the high cost of the ultrahigh vacuum chamber and the extremely slow film-forming rate. MBE is mainly used to study the growth process of ZnO thin films [30].

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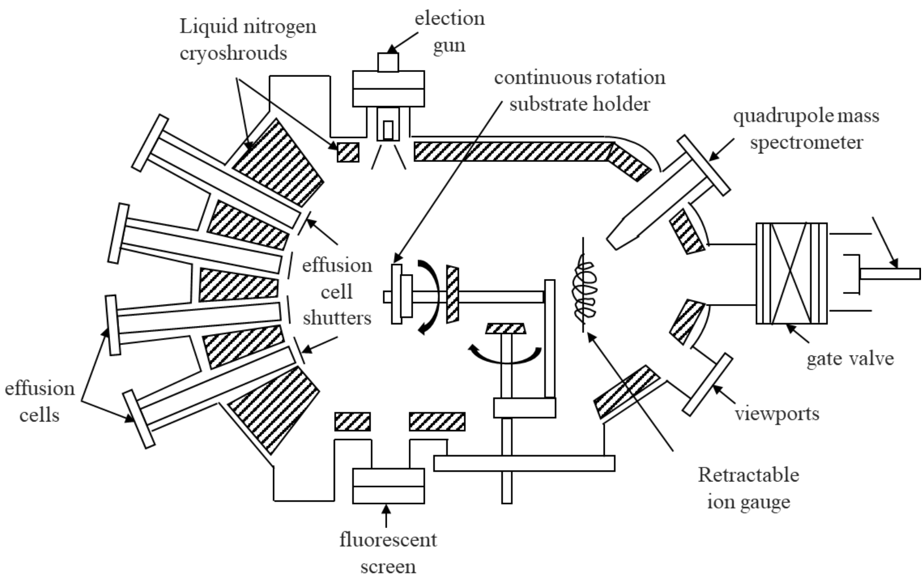

Figure 4. The principle of molecular beam epitaxy.

3.4. Magnetron sputtering

The thin film can be prepared by spin coating through specific chemical reactions, and the basic principle is as follows: after dissolving metal alkoxides related to film components in solvents to form homogeneous systems, the metal cations are hydrolyzed and condensed to form complexes, thus forming a metal-oxygen-metal network structure, and the solution is gradually transformed into a gel. Subsequently, placed the gel on the substrate, uniformly coated by high-speed rotation, and a thin film can be obtained by heating the gel, as shown in Figure 5 [1, 4, 27, 31].

Thin film prepared by spin coating has high uniformity, accurate stoichiometry and low reaction temperature. At the same time, this type of thin film has high repeatability because the thickness of the film can be controlled by adjusting spin speed, spin time and solution viscosity, and the composition of the film can be controlled by raw materials and modifiers in the solution system, which mean that it can be widely used in laboratory research and industrial production.

The disadvantage of spin coating is that the fine structure of the film cannot be controlled, and the compactness of the film is low. MOTFT based on ZnO, In_2O_3, ITO and IGZO can be produced by spin coating. With the development of technology, sol-gel has already achieved initial industrialization. Samsung has used sol-gel to prepare IZO film and drive a 2.2-inch AMOLED by the film [32].

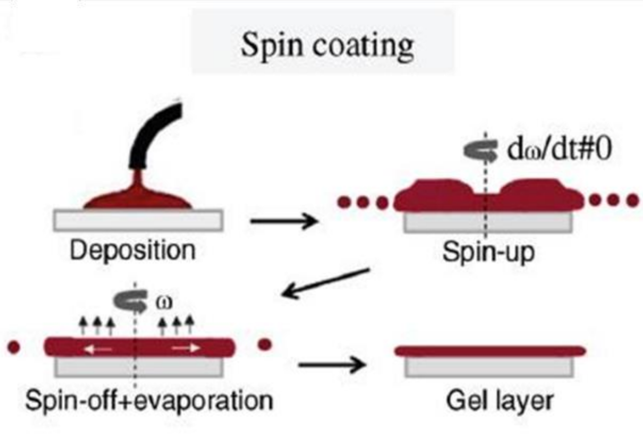

Figure 5. The principle of spin coating [27].

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3.5. Spray coating

Spray coating is similar to spin coating. The basic principle is as follows: After dissolving metal alkoxides related to film components in solvents to form homogeneous systems, the metal cations are hydrolyzed and condensed to form complexes, and the solution gradually transforms into the gel. Then, deposit the gel on the substrate surface in the form of aerosol by ultrasonic atomization or carrier gas injection. At last, the thin film can be obtained by heating gel deposited on the substrate, as shown in Figure 6 [4, 7, 27, 33]. The characteristics of spray coating are similar to those of spin coating, which has the advantages of a simple process, easy control of composition and doping modification, and can produce large-area oxide films, but has the disadvantage of the low density of production films. By contrast, spray coating's utilization rate of raw materials is higher.

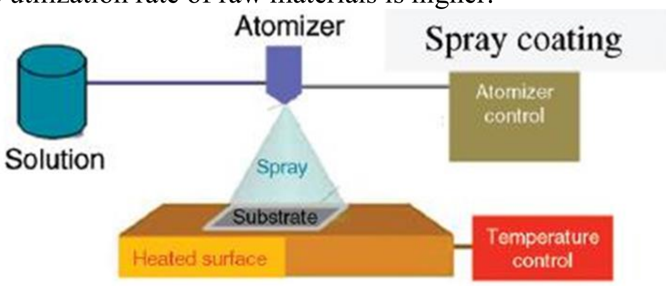

Figure 6. The principle of molecular spray coating [27].

3.6. Low-temperature solution-processing

Because of obtaining a dense oxide active layer film requires a heat treatment of nearly 400 °C. It requires a long time of heat preservation to improve the electrical stability of the film, which limits the application of spin coating and spray coating in the field of flexible electronics; low-temperature solution-processing develops based on these two methods, and the basic principle is as follows: The oxidant and reducing agent are added to the gel, and the heat released by the redox reaction and the heat provided externally is used to promote the condensation reaction. Alternatively, use UV irradiation gel to remove carbon-containing impurities in the system to promote a condensation reaction. Thereby realizing low-temperature (usually 200~250°C) liquid phase preparation [33].

The characteristics of low-temperature solution processing are similar to those of spin coating and spray coating. Meanwhile, it can obtain high-performance active layer films at lower annealing temperatures and has a good application prospect in the field of flexible electronic equipment. MOTFTs based on In_2O_3, IZO and IGZO can be produced by low-temperature solution processing. They all have good mobility and threshold voltage [34].

4. Application

MOTFT has the characteristics of high carrier mobility, good uniformity of oxide semiconductor thin films, low processing temperature, transparency to visible light, etc.

4.1. Display screen

ITO materials are typical in MOTFTs. Due to the width of the oxide thin films' forbidden band being large, they are transparent in the visible light range. Therefore, a transparent display is another potential application of oxide thin film transistors in the display. Due to the continuous progress of MOTFT technology, many companies worldwide, such as South Korea's Samsung Corporation and Taiwan's AUO Corporation, use TFT-driven display screens. Due to the high mobility and stability of MOTFT, it is an option for manufacturing large-size, high-frame rate displays. Excellent candidates for advanced LCD TVs with high pixel density, with broad market prospects in the commercial field [35, 36].

4.2. Flexible electronics

Flexible flat-panel displays and wearable devices are receiving extensive attention, and MOTFTs have been developed in the field of flexible electronic devices due to their high mobility and good chemical stability. Thin films are naturally flexible, and increasingly electronic products now require wearables, such as skin tattoos, flexible sensors, etc. [29], reported nearly 20 years ago, realizing flexible displays with certain reliability and lifespan [37]. Since Samsung developed the first IGZO-based TFT flexible backplane AMOLED screen in 2012, the flexible device has been used in a series of commercial applications. In 2013, the US MC10 company's first flexible device had medical detection function, and China BOE produced large-scale flexible devices in 2014. Increased companies are researching and developing image arrays on curved or flexible substrates [36, 38].

In addition to flexible displays, flexible electronic paper has also been extensively studied because metal oxide thin film crystals have high light transmittance and high mobility and can be fabricated at lower temperatures. From the emergence of a-IGZO TFT black and white electronic paper in 2005 to the large-scale production of high-performance OTFTs in 2021, flexible active drives will also become a major development highlight in the future (Figure 7) [39].

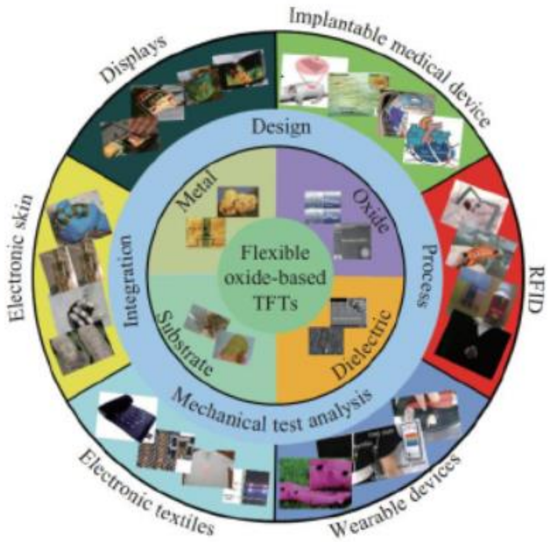

Figure 7. Application of flexible OTFTs [39].

5. Conclusion

This paper briefly describes the development history of MOTFT, focuses on the active layer semiconductor materials and preparation methods of MOTFT, summarizes the application of MOTFT in its advantageous fields, and makes an outlook on its development direction.

After experiencing single-component and multi-component oxides, composite oxides gradually become the protagonists of active layer materials. Oxide semiconductor materials are currently developing in the direction of high electron mobility through doping modification and the composite type and are gradually applied to a wider range of electronic devices; The new material of cellulose grid has also entered our field of vision, and they will certainly have a wider range of applications in the future and will continue to promote scientific progress in this direction.

With the development and progress of active layer media, the preparation method of active layer film has also been improved and developed accordingly. The spin coating belongs to the chemical synthesis molding method, and its preparation process is simple and suitable for large-area film production. The spray coating method is similar to the solution-gel method, but the compactness of the film produced is low. In order to prepare more stable, higher mobility and transparent thin film transistors, scientists have created magnetron sputtering, pulsed laser deposition, electron beam evaporation and other preparation methods. Furthermore, in the continuous improvement, scientists have also created a method of low-temperature solution treatment, which can obtain higher performance active layer films at lower annealing temperatures, which has very good development prospects in the field of flexible electronics. It is also hoped that all around the world can invent a greener and more environmentally friendly preparation method in the future.

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