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Commentary

A Fundamental Reason for the Need of Two Different Semiconductor Technologies for Complementary Thin-Film Transistor Operations

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Abstract: In this short commentary, we discuss a fundamental reason why two different semiconductor technologies are needed for complementary thin-film transistor (TFT) operations. It is mainly related to an energy-level matching between the band edge of the semiconductor and the work-function energy of the metal, which is used for the source and drain electrodes. The reference energy level is determined by the energy range of work-functions of typical metals for the source and drain electrodes. With the exception of silicon, both the conduction band edge (E_C) and valence band edge (E_V) of a single organic or inorganic material are unlikely to match the metal work-function energy whose range is typically from −4 to −6 eV. For example, typical inorganic materials, e.g., Zn–O, have the E_C of around −4.5 eV (i.e., electron affinity), so the conduction band edge is within the range of the metal work-function energy, suggesting its suitability for n-channel TFTs. On the other hand, p-type inorganic materials, such as Cu–O, have an E_V of around −5.5 eV, so the valence band edge is aligned with metal work-function energy, thus the usage for p-channel TFTs. In the case of p-type and n-type organic materials, their highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) should be aligned with metal work-function energy. For example, p-type organic material, e.g., pentacene, has a HOMO level around −5 eV, which is within the range of the metal work-function energy, implying usage for p-channel TFTs. However, its LUMO level is around −3 eV, not being aligned with the metals' work-function energy. So it is hard to use pentacene for n-channel TFTs. Along with this, n-type organic materials (e.g., C60) should have HOMO levels within the typical metals' work-function energy for the usage of n-channel TFT. To support this, we provide a qualitative and comparative study on electronic material properties, such as the electron affinity and band-gap of representative organic and inorganic materials, and the work-function energy of typical metals.

Keywords: thin-film transistors (TFTs); organic semiconductors; inorganic semiconductors; electron affinity; band-gap; metal work-function energy; complementary TFT operation

1. Introduction

Complementary metal-oxide-semiconductor (CMOS) technology is a mature and traditional device technology, especially for non-display applications [1]. Here, the single type of the semiconductor, which is silicon, can be employed for both n-channel and p-channel metal-oxide-semiconductor field-effect transistors (MOSFETs), and thus the CMOS operation. This is possible because silicon has proper energy-band properties in terms of a band-gap (~1.1 eV) and conduction band minimum energy (i.e., an electron affinity of −4.05 eV), and thus a valence band maximum energy of 5.15 eV [2]. Additionally, these unique properties allow both electron conduction for n-channel devices and hole conduction for p-channel devices through the metal electrodes where these carriers are collected by

minimizing rectification and interference. In other words, it can fit various metals with different work-function energies whose range are typically form −4 to −6 eV [3]. Essentially, the conduction band minimum (E_C) and valence band maximum (E_V) of silicon are within this work-function energy range of typically available metals.

However, CMOS technology has shortcomings when it comes to flexible/transparent electronics. Due to the necessity of a high-temperature process for CMOS technology, using flexible/transparent substrate (e.g., plastic) with low melting-points is almost impossible. So, to build electronic circuits on those substrates for transparent electronic systems or wearable devices, thin-film transistors (TFTs) based on room-temperature-processable or solution-processable non-silicon semiconductors (such as organic semiconductors and inorganic semiconductors represented by metal oxides) have been studied [4–8]. Different from display applications, both n-type and p-type transistors are necessary for performing complex functions and constitute circuit blocks. Unfortunately, unlike silicon, neither organic materials or inorganic materials are solely usable for both n-channel and p-channel thin-film transistors (TFTs) [9]. For instance, it is known that n-type inorganic and organic semiconductors, e.g., Zn-O and C60 are more favorable for electron transport, suggesting it for the n-channel TFTs. In contrast, p-type inorganic and organic materials, such as Cu-O and pentacene, better for the hole transport, are employed for p-channel TFTs. This implies that the conduction band of these n-type materials is only used for electrons while the valence band of p-type materials is only available for holes. Since the carrier transport within the semiconductor starts and ends at the metal electrodes at the source and drain, respectively, the metal property, e.g., work-function energy, should be associated with the TFT operation in terms of the type of main transport carrier. This technological issue of non-silicon-based TFTs is to be explained from a more fundamental point of view. In this paper, we present a theoretical discussion on a fundamental reason why two different semiconductor technologies should be employed for complementary TFT operations. It is mainly associated with an energy-level alignment between the band edge of the semiconductor and work-function energy of the metal incorporated as the source or drain electrode where the main transport carrier (e.g., electrons or holes) is supplied or collected. This suggests that both the conduction band minimum and valence band maximum of a single organic or inorganic material are unlikely to fit the work-function energy of typical metals. As the electron conduction material, n-type inorganic materials, e.g. Zn-O, have a high E_C and a very low E_V due to the wide band-gap. Here, E_C is only within the range of the available metal's work-function energy, so the conduction band edge can only be aligned with the metal electrode, suggesting its suitability as n-channel TFTs. Additionally, for n-type organic materials, e.g., C60, its E_C (i.e., lowest occupied molecular orbital, LUMO) is aligned with the metal work-function energy level, having n-rich material property. So this can be used for n-channel TFTs. In contrast to this, p-type organic semiconductors have a high E_V (i.e., highest occupied molecular orbital, HOMO), which is within the range of the metal work-function energy, so they are suitable for p-channel TFTs. Along with this, p-type inorganic materials, such as Sn-O, have an energy band whose E_V is only matched with a metal's work-function energy, thus a possibility of p-channel material. These imply that a complementary TFT operation is possible from a combination of these two different material families. Regarding these theoretical insights, we show a qualitative and comparative study on electronic material properties of some organic and inorganic materials and the work-function energy of some of the metals typically used in TFTs.

2. Comparative Table of Electronic Material Properties

Figure 1 shows a comparative table of basic electronic properties of inorganic materials, organic materials, and metals, While the inorganic or organic semiconductor materials are used as the channel layer in TFT structures, metals are used as the electrode at the source and drain terminals where the conduction path starts or ends through the semiconductor channel layer, providing the terminal current modulated with the insulated gate capacitor structure [10]. This section mainly focuses on these channel materials and metals in the TFT structure.

2.1. n-Type Inorganic Materials

As can be seen in Figure 1, firstly, n-type inorganic materials, represented by conducting oxides (e.g., Zn-O [11]), have a high electron affinity (χ_e) around −4.5 eV [12]. This determines the energy level of the conduction band minimum. Besides, due to the wide band-gap (E_g) of more than 3 eV [13], the valence band maximum is very low at around −7 eV measured from the vacuum energy (E_{vac}). Since the work-function energy of typical metals is within the range from −4 to −6 eV, only the conduction band edge of n-type inorganic materials is aligned with the metal which is used for an electrode in TFT structures.

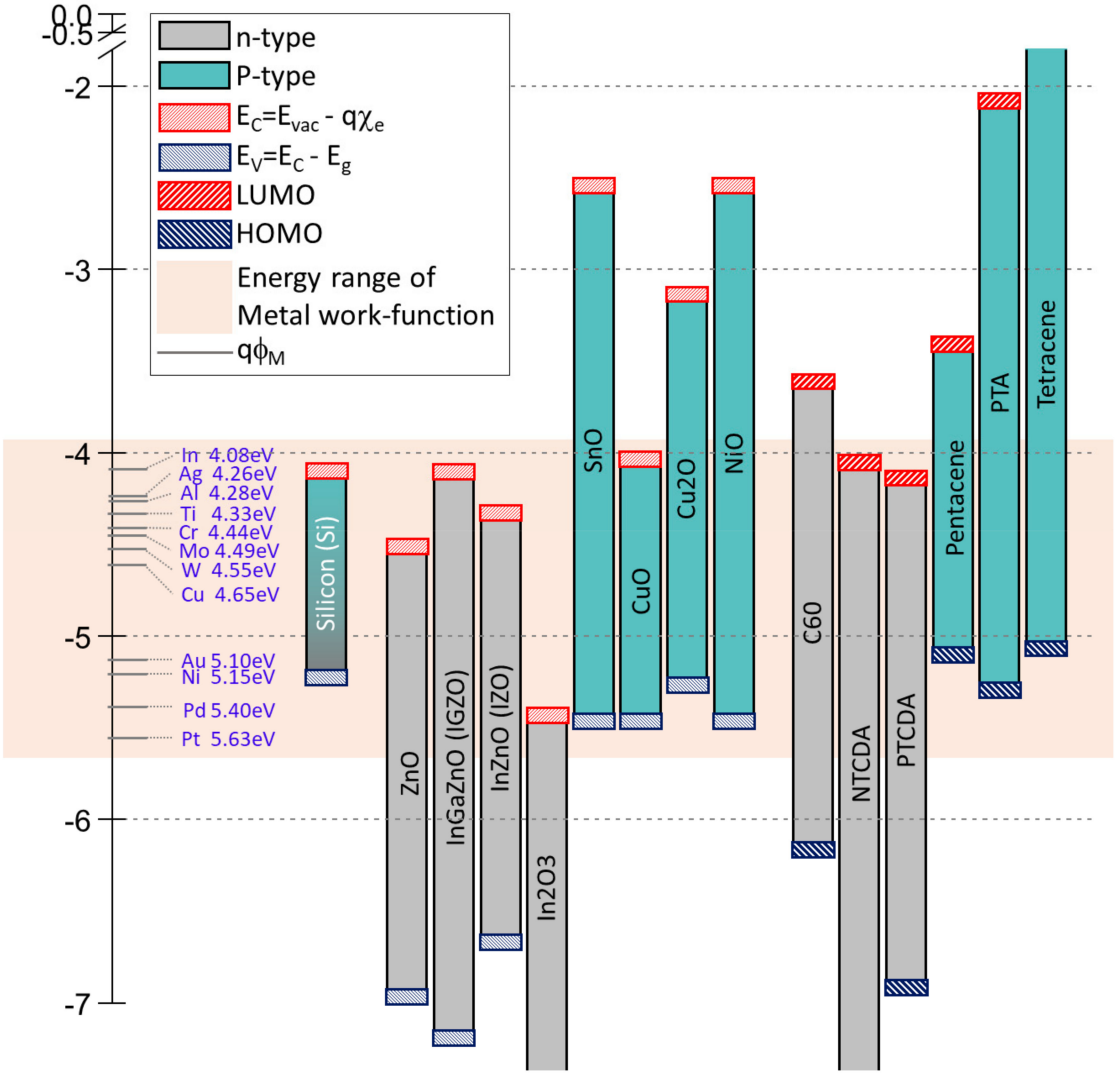

Figure 1. A graph compares energy band edge positions of n-type and p-type inorganic/organic semiconductor materials with a typical contact metal's work-function energy.

2.2. p-Type Inorganic Materials

P-type inorganic materials, such as Ni-O and Sn-O, have an E_V of around −5.5 eV and an E_C of around −2.5 eV [14,15], as shown in Figure 1. Since their E_V are within the range from −4 to −6 eV and their E_C are out of the range of typical metal, the valence band edge of p-type inorganic materials is only aligned with typical metals.

As can be seen in Figure 1, Cu-O has an E_V of around −5.5 eV, and an E_C of around −4 eV [16]. In this case, both E_C and E_V are within the range of typical metal's work-function energy, so it seems that it can be used for both n-channel and p-channel TFTs' channel material. However, due to its material

nature (e.g., high vacancy formation enthalpy, high degree of disorder near E_C), oxygen interstitials and copper vacancies contribute to a p-type conductivity, thus making it a p-type material [17,18].

2.3. p-Type Organic Materials

As shown in Figure 1, the HOMO level, equivalent to E_V, of typical p-type organic materials (e.g., pentacene) are around −5 eV from E_{vac}. However, the LUMO as E_C is located at around −3 eV, which is closer to E_{vac} by the amount of energy of E_g [19]. So, these properties make the HOMO level only aligned with the work-function energy of typical metals (i.e., ϕ_m from 4 to 6 eV).

2.4. n-Type Organic Materials

In contrast to the p-type organic materials, n-type organic materials' E_V (i.e., LUMO) is aligned with the work-function of the typical metals. As can be seen in Figure 1, n-type organic material C60 has LUMO level of −3.5 eV and HOMO level of −6.2 eV [20]. Besides, though both LUMO and HOMO can be aligned with each metal, p-type doping of C60 is difficult because of its high ionization energy [21]. So it can be used only for n-channel TFTs with proper doping.

2.5. Metals

As another key element in TFTs, metals are used as the source and drain electrodes where the carriers, e.g., electrons and holes, are collected forming the terminal current between the drain and source. As seen in Figure 1, the work-function energy of typical metals (e.g., In, Ag, Al, Ti, Cr, Mo, W, Cu, Au, Ni, Pd, Pt) are largely within the range of −4 to −6 eV. These metals have relatively high electrical strength and electronic stability in terms of bonding across the metal molecules, thus a low reactivity with an ambient condition. This suggests that these metals are stable enough to be used as the terminal electrodes. Note that there is an exception, i.e., sodium (Na), with work-function energy around −2.3 eV, which is too unstable and reactive to be used as the transistor's terminal electrode.

3. Carrier Transport through Semiconductors and Metals in TFTs

3.1. Electron Transport and n-Type Inorganic Materials with Metals

As discussed in the previous Section 2.1, the conduction band edge of n-type inorganic semiconductors is well aligned with the work-function energy of typical metals. This means that electron transport can be well established, especially with a n-type inorganic material. Figure 2a shows a horizontal band diagram along the channel length from the source to the drain. As seen here, electrons are supplied from the source metal, and travel through an inorganic material. Finally, they are collected at the drain metal, forming the terminal current. Here, it is noticed that the barrier height between the work-function energy level of the drain metal and E_V of the channel layer is too high to get the hole transport. So, a very high Schottky barrier height for holes exists, making this kind of semiconductor materials not suitable for p-channel (i.e., hole conduction) TFTs.

Besides, a degree of disorder of the conduction band in inorganic semiconductors is very low; thus, a Fermi level can be easily modulated by the gate field in TFT structures [22], with no significant interference in the carrier transport [23]. In oxide-based inorganic materials, oxygen vacancies formed during the film deposition process play the role of the electron donner; thus, an n-type conducting oxide is controlled by the amount of oxygen vacancies [24,25].

3.2. Hole Transport and p-Type Inorganic Materials with Metals

For the usage for p-channel TFTs, p-type organic materials should have E_V that is within the range of typical metal work-function energy, thus a hole transport. Figure 2b shows a horizontal band diagram of the source to the drain through the channel in the p-channel TFT. Holes supplied from the source are collected at the drain through the inorganic material. As we discussed in the previous section, Ni-O and Sn-O have a high E_v around −5.5 eV, matching the typical metal work-function

energy range, thus a hole transport. Its low E_c around −2.5 eV, however, makes it hard for the electrons to travel, forming a high Schottky barrier. Here, it is clear that hole transport is well established through the pentacene, while electrons transport poorly.

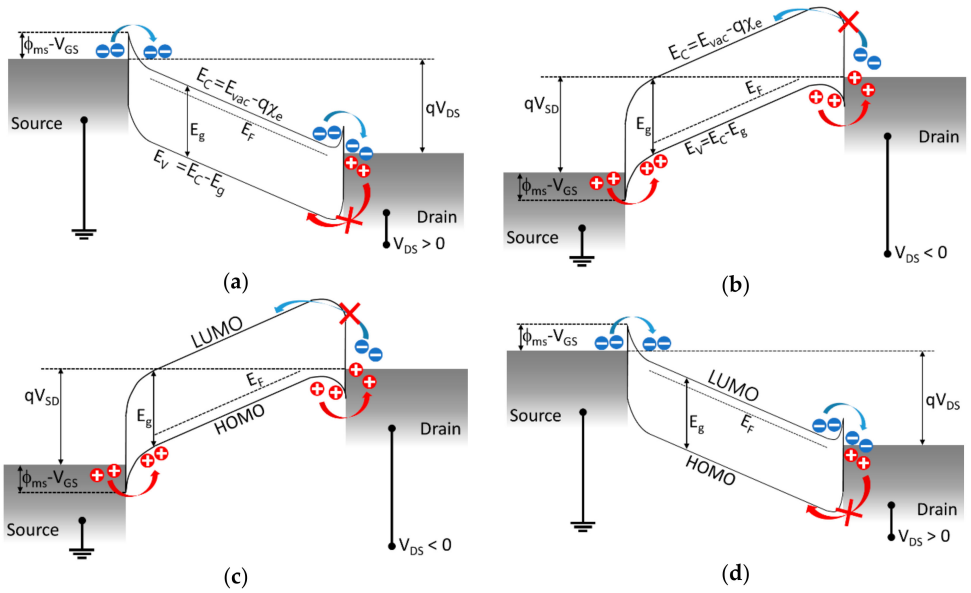

Figure 2. Energy band diagram along the channel from source to drain of the TFT, which is in on-state. (**a**) Inorganic n-channel TFT case with positive V_{GS} and V_{DS}. The electrons are traveling well while the holes are facing the high barrier. (**b**) Inorganic p-channel TFT case with negative V_{GS} and V_{DS}. The holes transport through the channel, but the electrons are blocked by the high barrier. (**c**) Organic p-channel TFT case with negative V_{GS} and V_{DS}. Only the hole conduction is established as well as the inorganic p-channel TFT case. (**d**) Organic n-channel TFT case with positive V_{GS} and V_{DS}. Only the electrons travel along the channel; likewise, the case of inorganic n-channel TFT.

Here, CuO has an E_C and an E_V that can both be aligned with typical metal work-function. From this point of view, it seems that both electron and hole conduction can be established. However, as discussed in the previous Section 2.2, due to its material nature, the number of free electrons is very small, thus a poor conductor for the electrons.

In this type of oxide semiconductors, sub-gap tail states near the conduction band, known to originate mainly from defects such as metal vacancy, contribute to the hole concentration. This also traps electrons, thus being a well-established hole transport and poor electron transport [26].

3.3. Hole Transport and p-Type Organic Materials with Metals

The valence band edge (i.e., HOMO) of p-type organic materials, e.g., typical polymers, is well-matched with the work-function energy of metals, as discussed in the previous Section 2.2. This suggests that the hole transport can be made. As seen in Figure 2c, the horizontal band diagram describes that holes are traveling from the source metal to the drain metal, and the intermediate medium is a p-type organic semiconductor. As can be seen, holes can overcome the barrier between the metal and E_V (i.e., HOMO), while electrons face a high barrier height. Within the organic semiconductor, the number of holes are modulated by the position of the Fermi level externally controlled by the gate field. Note that the density of states for the valence band has a Gaussian profile where holes are hopping through [27].

3.4. Electron Transport and n-Type Organic Materials with Metals

In the n-type organic material case, the conduction band edge (i.e., LUMO) should be matched with the metal work-function energy. See Figure 2d for the horizontal band diagram of n-type organic

channel TFT. Electrons are supplied from the source, traveling through the organic material, collected at the drain, thus forming terminal current. Along with other cases in this section, electrons easily overcome the barrier between the metal and semiconductor, while holes face high barriers, thus only the electrons transport. However, there are n-type organic materials whose HOMO and LUMO can both be matched with the metal work-function range, such as C60. Unfortunately, p-type doping of C60 film is difficult due to its high ionization energy.

Here, the main mechanism of electron transport in n-type organic material is hopping conduction [28]. Additionally, the charge-carrier states are disordered with a Gaussian profile. [29].

4. Summary

We have discussed a fundamental reason for the need of two different materials for a complementary operation of TFTs. There are several possible combinations, such as n-type and p-type organics [30], n-type and p-type inorganics [31], n-type inorganics and p-type organics [32,33], and n-type organics and p-type inorganics (even with the inefficient combination). Along with the limited range of metal work-functions, only one of the conduction band and valence band edges is aligned with the work-function energy level of typical metals. This essentially determines a suitability to be used as an n-channel or p-channel material regardless of whether it is an organic or inorganic material. Consequently, this work can be a good basis for the selection of materials and their combinations for an n-channel or p-channel TFT.

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