



# An amorphous oxide semiconductor thin-film transistor route to oxide electronics



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## ABSTRACT

Amorphous oxide semiconductor (AOS) thin-film transistors (TFTs) invented only one decade ago are now being commercialized for active-matrix liquid crystal display (AMLCD) backplane applications. They also appear to be well positioned for other flat-panel display applications such as active-matrix organic light-emitting diode (AMOLED) applications, electrophoretic displays, and transparent displays. The objectives of this contribution are to overview AOS materials design; assess indium gallium zinc oxide (IGZO) TFTs for AMLCD and AMOLED applications; identify several technical topics meriting future scrutiny before they can be confidently relied upon as providing a solid scientific foundation for underpinning AOS TFT technology; and briefly speculate on the future of AOS TFTs for display and non-display applications.

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## 1. Introduction

Oxide electronics is a very diverse and active field, encompassing materials such as dielectrics, ferroelectrics, magnetics, piezoelectrics, multiferroics, high-temperature superconductors, epitaxial oxides, memories, and/or sensors. These materials find interest and application in a myriad of devices ranging from high-density memories to large-scale sensor arrays. In this contribution, we focus on a branch of oxide electronics that often employs monikers such as 'oxide thin-film transistors' or 'oxide TFTs'. This topic can be further subcategorized by specifying whether the microstructure of the TFT channel layer is amorphous or polycrystalline. We will confine our attention to a specific class of amorphous channel layer materials, amorphous oxide semiconductors (AOS).

Our AOS TFT topical choice is primarily motivated by flat-panel display considerations. The dominant flat-panel display technology – active-matrix liquid crystal display (AMLCD) – would benefit from a higher performance channel layer replacement for amorphous hydrogenated silicon (a-Si:H), as is currently used in switching TFTs for backplane pixels. Such a replacement, however, should not entail a substantial cost penalty. AOS TFTs are very attractive

candidates for a-Si:H TFT replacement. The amorphous nature of an AOS TFT is a key advantage. Using the success of a-Si:H TFTs as a guide, amorphous materials are more readily and economically scaled to the exceedingly large dimensions ( $\sim 9 \text{ m}^2$ ) required for AMLCD high-volume manufacturing. As AOS TFTs are successfully integrated into AMLCD backplanes, other flat-panel display applications such as organic light-emitting diodes, electrophoretic displays, and transparent displays may well follow. While AOS TFT development is currently driven by the needs of the flat-panel display industry, other large-area or conventional silicon-based electronics applications could emerge, depending on the performance, reliability, and manufacturability of AOS TFTs as established by their use in commercial displays.

This paper is organized as follows. Section 2 is devoted to AOS materials design considerations that motivate the emergence of indium gallium zinc oxide (IGZO) as the current AOS commercial material-of-choice and provide a framework for undertaking future AOS material selection and design. In Section 3, the case for IGZO TFT implementation into next-generation AMLCDs is presented. In Section 4, the more challenging task of employing IGZO TFTs into AMOLEDs is addressed. In Section 5, several questions are posed for the AOS research community regarding fundamental scientific/technical issues that, in our view, are not resolved and need to be more adequately addressed. In Section 6, we offer conclusions and perspectives on the future of AOS technology for display and other emerging applications.

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## 2. Amorphous oxide semiconductor (AOS) design

The portion of the periodic table, highlighted in Fig. 1, was proposed by Hosono et al. in 1996 as a starting point for choosing multicomponent combinations of cations for the design of AOS [1]. Prior to initiating a discussion of AOS design, two historical footnotes are warranted. First, these AOS guidelines were originally formulated for the design of transparent conductive oxides (TCOs) in contrast to their application as TFT channel materials per the focus of our discussion here. The notion of using these prospective TCO materials in a TFT channel application was in fact quite non-obvious, as witnessed by the nearly one decade delay before the first AOS based TFTs were demonstrated. The desirable traits for a candidate TCO material are substantially different than those for an AOS channel material, given the nature and constraints of their respective applications, and the recognition of the potential for high-performance AOS based TFTs in the early 2000s generated a great deal of excitement in the technical community. Second, in early publications, AOS materials designed according to Fig. 1 guidelines were referred to as amorphous multicomponent heavy-metal cation oxides. Since 'heavy metal' connotes toxicity in conventional English usage, today these materials are referred to as AOS.

Returning to AOS design, Hosono et al. advocated selecting cations from the portion of the periodic table shown in Fig. 1 since materials, designed using such cations, possess conduction bands derived from large ionic-radius, spherically symmetric 4s, 5s, or 6s electron orbitals [1]. These orbitals lead to a high degree of wave-function overlap, electron delocalization, and relatively high electron mobility, independent of whether the microstructure is crystalline or amorphous. Simple binary oxides such as ZnO, SnO<sub>2</sub>, and In<sub>2</sub>O<sub>3</sub> have a strong tendency to crystallize. This can be circumvented by specifying that cations selected from the portion of the periodic table shown in Fig. 1 should be combined in multicomponent systems to confuse the lattice as to which structure type to adopt, thereby frustrating crystallization. The simplicity and viability of these design guidelines has contributed greatly to the success of AOS.

Now consider implications of the elemental color-coding scheme adopted in Fig. 1. Of the fifteen elements proposed in Fig. 1, five of them (As, Cd, Hg, Tl, Pb; red) are avoided by most researchers because of their toxicity, three of them (Cu, Ag, Au; brown) are possibly useful for the design of a p-type semiconductor (since our current emphasis is on n-type AOS design, these elements will be eliminated from further consideration), and three of them (Ge, Ag, Au; orange) are less attractive options because of their high cost. Eliminating these elements from further consideration, six elements remain of the initial fifteen. Four of them (Zn, Ga, In, Sn) are colored blue; they are the elements most commonly used in AOS design. The other two (Sb, Bi; black) may eventually

11	12	13	14	15	
29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	4
47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	5
79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	6

Fig. 1. The portion of the periodic table for selecting amorphous oxide semiconductor cations. Color coding: blue = most common cations employed in AOS design, red = toxic, brown = p-type cations, orange = high cost cations, black = largely uninvestigated.

prove to be appropriate AOS cation choices, but their usefulness has apparently not yet been validated in the literature. Further inspection of the detailed color-coding scheme employed in Fig. 1 reveals that cost is also of some concern with respect to Ga and In, while In is sometimes classified as toxic. Since cost is often related to elemental abundance and/or world-wide production, these properties as well as toxicity are compared in Table 1 for the four most common AOS cations. It is very clear from Table 1 that Zn and Sn are the two most attractive AOS cation choices from the perspective of abundance, cost, world-wide production, and toxicity.

Briefly, we now constrain our AOS design discussion to the use of Ga, In, Sn, and/or Zn cations for TFT channel layer applications [5–8]. The past decade of intense worldwide research has established a framework whereby the contribution of each of these cations to overall AOS TFT channel performance can be nicely rationalized. In, Sn, and Zn are intriguing AOS design starting points since their binary oxides – In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and ZnO – are the three most commonly used TCOs. The small effective masses and corresponding relatively high mobilities of these oxides are valued for both TCO and AOS applications. However, TCO applications require high electron concentrations ( $\sim 10^{20}$ – $10^{21}$  cm<sup>-3</sup>), whereas an optimized AOS for use as a TFT channel layer must have a small electron concentration, preferably  $< 10^{16}$  cm<sup>-3</sup>. Incorporation of In and/or Sn (to a lesser extent) in an AOS tend to increase the electron concentration. In contrast, inclusion of Zn and especially of Ga will lead to a suppression of the electron concentration. Unfortunately, use of Ga in an AOS also tends to reduce its mobility.

The tendency for a given cation in an AOS to increase or suppress the electron carrier concentration can be rationalized by reference to the atomic solid-state energy (SSE) scale given in Fig. 2 [9,10]. The SSE for a given element constitutes an estimate of its frontier orbital energy position with respect to the vacuum level when it is incorporated into an inorganic solid. Cation and anion behavior are distinguished by the SSE position with respect to  $-4.5$  eV, a universal energy reference corresponding to the hydrogen donor/acceptor ionization energy [ $\epsilon(\pm)$ ] or, equivalently, to the standard hydrogen electrode (SHE) potential of electrochemistry as measured with respect to the vacuum level. Because SSE for a cation equates to the average electron affinity (EA) of a series of binary compounds, it is important to note that the EAs for In<sub>2</sub>O<sub>3</sub>, SnO<sub>2</sub>, and ZnO are reported to fall in the range of  $-4.4$  to  $-4.6$  eV. These values are positioned very near  $\epsilon(\pm)$ , an energy where electron doping is energetically favorable. For Ga<sub>2</sub>O<sub>3</sub>, however, EA =  $-3.1$  eV, i.e., it is energetically separated from  $\epsilon(\pm)$  by 1.4 eV. At this energy, Ga becomes an electron-suppressing cation. These SSE trends are also consistent with the occasional use of Al and Hf in AOS as electron-suppressing cations [11–13], since SSE (Al) =  $-3.1$  eV and SSE (Hf) =  $-2.0$  eV are energetically positioned well above  $\epsilon(\pm)$ .

In addition to mobility-enhancing/degrading and electron-creating/suppressing tendencies, two other cation properties may be relevant for future AOS selection/design purposes. First, the wet etching characteristics of an AOS contribute to its process integration compatibility when it is used in a thin film. Ga, In, and especially Zn are easily etched by wet methods, while Sn can present significant challenges. Thus, if an application requires increased selectivity in which the AOS is made harder to etch, the addition of Sn is likely. Second, since Ga and In melt at very low temperatures (30 and 150 °C, respectively) compared to Sn and Zn (232 and 420 °C, respectively) it is unlikely that Ga- or In-containing metal sputter targets can be fabricated. Thus, sputtering of Ga- or In-containing AOS will require the use of ceramic targets. In contrast, ZTO sputtering can be accomplished via reactive sputtering using a metal target.

Based on these guidelines, AOS designs using Ga, In, Sn, and/or Zn can be comprehensively categorized as follows, recognizing that

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