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Orgin of Subgap Features in Transparent Amorphous Oxide Semiconductors

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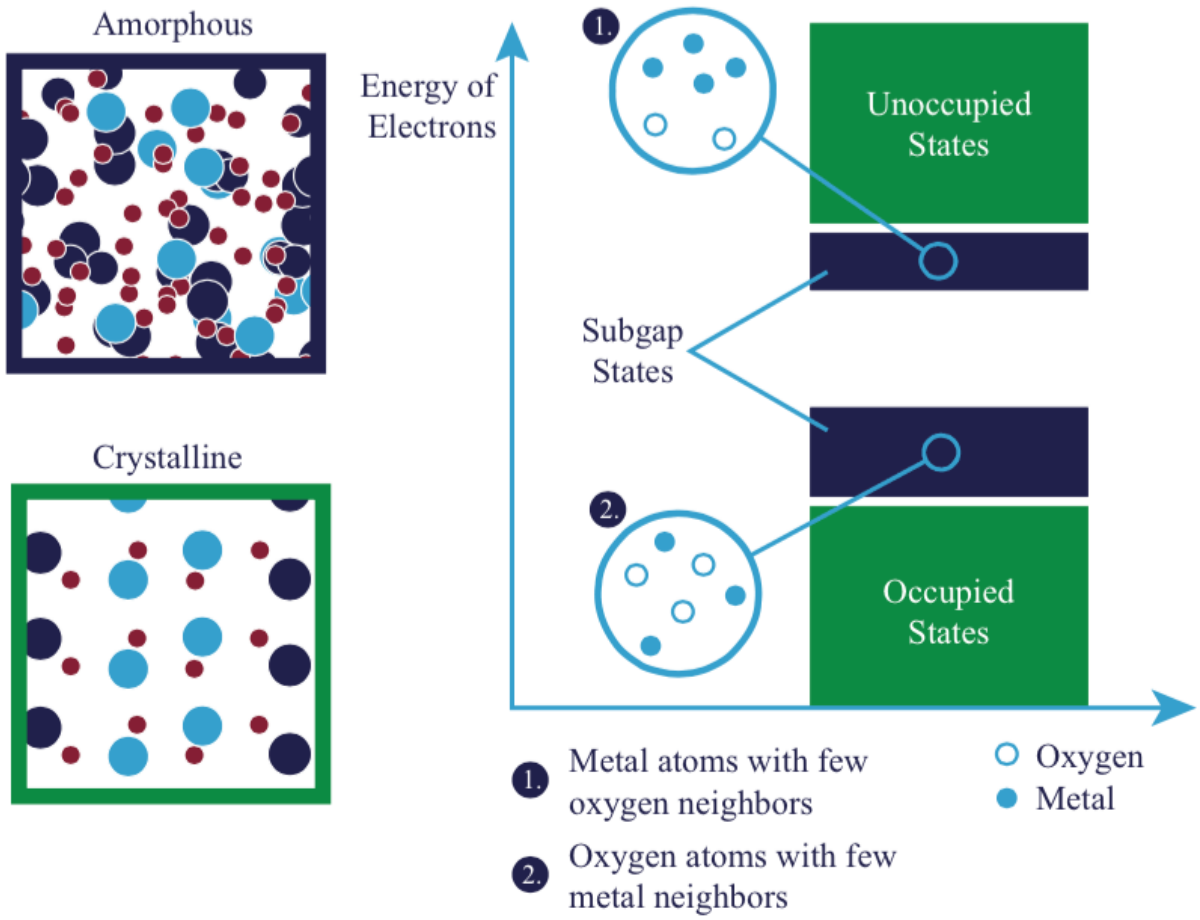
Abstract
Amorphous indium gallium zinc oxide (a-IGZO) is a transparent amorphous oxide semiconductor (TAOS) that has shown promise as transparent thin film transistors (TTFTs) in various display applications. Within a-IGZO films, states can form in the band gap that hinder TTFT performance. In order to elucidate the origin of these states, we examined the formation of the subgap states for a-IGZO thin films with various compositions. We observed a positive correlation between the subgap formation and the percentage of oxygen ruling out oxygen deficiencies as a factor in the formation of subgap states. Furthermore, metallic indium crystallites were observed to form for samples grown in oxygen deficient conditions. Our studies reveal that subgap states are due to oxygen with few surrounding metal neighbors and indium with few surrounding oxygen neighbors. The subgap states can be suppressed in a-IGZO (and other TAOS) by careful choice of composition.

Transparent amorphous semiconducting oxides (TAOS) have gained widespread interest due to their compatibility with large scale growth methods including roll-to- roll processing.(Yu et al., 2012) In particular, amorphous indium gallium zinc oxide (or a-IGZO) has attracted significant attention due to its high electron mobility com- pared to amorphous silicon.(Nomura et al., 2004) Already, a-IGZO has shown promise for use in active-matrix organic light-emitting diodes (AMOLEDs) which can allow for thinner displays with increased power efficiency. Although only small scale pro- totype displays have been produced, the devices have shown reasonable uniformity of a-IGZO transparent thin film transistors (TTFTs) suggesting larger high quality AMOLED displays are possible.(Jeong et al., 2008)



- Crystalline IGZO is a transparent conductor formed at high temperatures
- Amorphous IGZO can be grown at room temperature
- Additional states appear because of disorder that harms transparency
- We have shown that metal and oxygen atoms with fewer opposite nearest neighbors are the cause

Figure 1 . Summary graphic on the experimental findings for the origin of the subgap features.

Compared to its crystalline form, a-IGZO displays some additional states within its forbidden energy band gap. The band gap is the energetic separation between the highest energy states filled with electrons and lowest energy states without electrons. Transitions can occur between the highest occupied states and the lowest unoccupied states with the absorption of any light with an energy greater than the band gap. The energy difference will then determine what light is transmitted and absorbed when passing through a material. For transparent applications, a

wide band gap is desirable as it leads to transparency in the visible range. The subgap states within the band gap can lead to additional transitions of lower energy and potentially lead to the absorption of visible light. Therefore the subgap states can lead to a decrease in transparency and coloration of thin films.

Additionally, subgap states can be detrimental to device performance by con- tributing to negative bias stress instability under illumination.(Nomura, Kamiya, & Hosono, 2011) For an a-IGZO TTFT, there is a certain applied voltage required for operation. Without any light illumination, the voltage remains constant over time and the device is stable. With light illumination including visible light, the voltage significantly changes over time with the creation of subgap states.(Oh et al., 2010) The creation of these subgap states and the changing voltage limits the long term stability of devices.

In order to increase the viability of a-IGZO for flexible electronics and commer- cial display devices, improvements are needed in roll-to-roll processing focusing on high quality and inexpensive thin film growth.(Wager & Hoffman, 2011) For further development of a-IGZO TTFTs, a greater understanding of the microscopic origin of the subgap feature is needed. Oxygen vacancies are often invoked to explain the subgap features but a vacancy is a vague term for amorphous solids with a disor- dered structure.(Oh et al., 2010; Nomura et al., 2011) Here, we comment on our recent publications on the origin of the subgap states of a-IGZO.(Sallis et al., 2014, 2015) These studies identified two types of subgap state that can exist, which arise from either under-coordinated oxygen or metal atoms. This work prompted the idea that the choice of composition can be used to suppress subgap formation. Here, we discuss the implications of this finding for other TAOS candidates and explain how it led to our latest studies of an indium-free TAOS absent of subgap states i.e. tin monoxide.(Wahila et al., 2015)

A series of a-IGZO thin films were grown under various conditions at the Nanofabrication Laboratory in Binghamton. We employed a combination of trans- mission electron microscopy (TEM) to examine the local atomic structure and x-ray photoelectron spectroscopy (XPS) to determine the elemental composition and inten- sity of subgap states near the surface of a-IGZO thin films. Changes in the intensity of the subgap features were examined upon modifying the surface and bulk properties with argon sputtering and low temperature vacuum annealing.

Under oxygen-poor growth conditions, XPS revealed the emergence of an ad- ditional indium species. Closer examination of the TEM images revealed these were metallic indium crystallites.(Sallis et al., 2015) The metallic indium forms with few oxygen neighbors (undercoordination) and leads to the formation of subgap states below the lowest unoccupied states.

Further analysis of over 50 samples revealed a positive correlation between the intensity of the subgap states above the highest occupied states and the oxygen composition.(Sallis et al., 2014) The positive correlation indicates that this subgap feature is not related to oxygen deficiency. Atomistic electronic structure calculations, performed by collaborators at Bath University, were used to theoretically calculate the electronic band structure and density of states near the band gap. The atomistic calculations showed that subgap states may form in stoichiometric a-IGZO indicating the subgap feature does not correspond with oxygen vacancies. Furthermore, the atomistic calculations imply the subgap feature is directly related to the environment surrounding the oxygen and increases with a lower coordination number.

Figure 1 summarizes our findings from two of our published articles focusing on the undercoordinated oxygen (Sallis et al., 2014) and under coordinated indium.(Sallis et al., 2015) Both the crystalline and amorphous structures are shown in the figure. In the crystalline form,

atoms are arranged in a repeating pattern surrounded with a set number of neighbor atoms. In amorphous materials, the disordered structure can lead to variation in both the number of neighbor atoms and the separation distance. In a-IGZO, when oxygen has fewer metal neighbors, a new state forms above the edge of the occupied states. Additionally, when indium has fewer oxygen neighbors, a new state forms below the edge of the unoccupied states.

The studies revealed that desired electrical properties of TAOS can still be ob- tained without producing subgap states by careful choice of composition. In order to investigate the electronic properties of thin film oxides with earth abundant ele- ments, we are examining amorphous tin oxides for the formation of subgap states. Our current studies indicate the subgap feature is observed in tin dioxide (SnO2) but absent in tin monoxide (SnO). The tin to oxygen ratio of tin monoxide reduces the likelihood of oxygen with too few metal neighbors, thereby suppressing the sub- gap formation.(Wahila et al., 2015) The absence of the subgap feature may allow tin monoxide to be a hole conducting TAOS, which will have significant consequences for the development of transparent and flexible logic devices.

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