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Review

Prospects and challenges of perovskite type transparent conductive oxides in photovoltaic applications. Part I – Material developments

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A B S T R A C T

Transparent conductive oxides (TCOs) have been used in a wide variety of applications as sensors and electronic displays and for solar harvesting for the past decades. TCOs are made of conductive materials such as metals. Many studies have been conducted to improve the properties of materials for TCOs. The properties that make a TCO effective are high transmittance and low resistivity. The current commercialized TCO is indium tin oxide (ITO), which has excellent transmittance and lower resistivity than other TCOs such as zinc oxide. Indium is expensive as its availability is becoming more limited over time. As such, studies to find an alternative material to ITO are continuing. Perovskite-structure materials are a candidate material with acceptable optoelectric properties. Perovskites have a wide band gap of ~3.0 eV and high transmittance along with exceptionally low resistance. The first part of this paper mainly discusses the progress and development of perovskite-structured TCO as well as materials modification by doping.

Contents

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1. Introduction

Presently, transparent conductive oxides (TCOs) serve in a wide variety of applications including devices such as screen panels for televisions, sensors, solar cells, and even photovoltaic windows (Boscarino et al., 2014; Knapp et al., 2011; Principato et al., 2010; Stadler, 2012). TCOs are materials that are conductive and at the same time exhibit a transparent characteristic that allows light to pass through the material itself. TCOs are a type of very thin film that is usually deposited on different substrates. Substrates used in solar applications are usually made from material with high transparency such as silica glass or fluorine tin oxide (FTO) glass in order to allow more light to penetrate the material to maximize efficiency (Izzi et al., 2015; Liu et al., 2015). The characteristics that are important for a TCO to be suitable for solar applications are the transmittance and sheet resistance. The TCO itself must also have a band gap energy of 3.1 eV or greater according to (Guillén and Herrero, 2011; Hoel et al., 2010), and the high band gap allows the TCO to transmit 80% of visible light or more (Bawaked et al., 2014; Bhachu et al., 2012; Sathasivam et al., 2015).

The material that is used commercially as a TCO is indium-doped tin oxide (ITO), due to its high transparency and low resistivity. However, the scarcity of indium has led to the material being expensive in terms of raw material cost and it is a toxic material (Dianetti et al., 2015; Hagendorfer et al., 2014; Minami, 2005; Sibiński et al., 2012; Sohn and Kim, 2011). On top of that, the ITO is often deposited on the substrate by physical vapour deposition (PVD) methods such as pulsed laser deposition (PLD) and radio frequency (RF) sputtering. These methods require extreme deposition conditions such as a high vacuum and high-end equipment, and thus they are a rather expensive means of deposition (Chen et al., 2013; Coutal et al., 1996). Since extreme conditions are a requirement for ITO fabrication, other cheaper methods such as chemical vapour deposition (CVD) are unsuitable. Due to the setbacks of ITO, researches have been conducted on other materials to substitute for ITO in the manufacture of TCOs for solar applications. FTO is another TCO that is widely used as an alternative to ITO and has a transmittance rivalling that of ITO. However, it has been mentioned in other literature that FTO has relatively low electrical conductivity and is much harder to pattern by wet etching compared to ITO (Liu et al., 2010).

Perovskite-structured materials are among the materials that are favoured as a candidate for a TCO. Perovskite oxides have attracted the attention of researchers due to their characteristics, which may make them suitable for use as TCOs. The structure of perovskite oxide has the general formula ABO_3, where A is a metal or organic cation and B is a metal cation (Song et al., 2015). According to Liu et al. (2008), perovskite-type oxides have properties such as superconductivity at high temperature and electro-optical effects. Usually, perovskites possess a wide band gap, thus allowing them to become a conductor at high temperatures.

The paper aim to discuss the materials development of perovskite-structured that have been performed to produce perovskite-type materials as TCOs. The modification materials through doping could improve the materials properties, which allow conductivity in the TCO itself. The combination of materials and dopant will produce a material that fulfils the requirements of an ideal TCO. The optoelectrical properties of main interest for a TCO are the transmittance and electrical resistivity.

2. Research progress on TCOs

TCOs are used as layers of solar cells or displays and are made of material with high transmittance and low resistivity. The material that is currently used commercially for TCOs is ITO, which is a colourless and highly transparent material as a film (Karasawa and Miyata, 1993; Laux et al., 1998; Paine et al., 1999; Stadler, 2012). However, ITO suffers from the scarcity of indium metal, which has led to an increase in its market price. Approaches have been carried out to improve the optoelectric properties of TCO using many different materials and deposition techniques with the aim of successfully compete with the current market TCO.

The earliest TCOs that have been widely produced in the past three to four decades other than ITO are zinc oxide, indium oxide (In_2O_3), and tin oxide (SnO_2). Researches are constantly being carried out to discover new materials with more favourable performance. The methods of producing thin films of TCOs are among the main concerns in tuning the performance of the materials, since different methods tend to give different results in terms of the performance of the TCO. Methods such as PLD, RF sputtering, spin coating, and electrospinning are among those used in the fabrication of TCOs (Timothy et al., 1999).

TCOs have also been made in the form of multi-layered thin films. Guillén and Herrero (2011) mentioned that it is viable to reduce the consumption of ITO by decreasing its thickness. When very thin ITO is used in combination with a thin metal such as Ag, Cu, or Au, which have resistivities of around $10^{-6}\ \Omega$ cm, a visible transmittance of 85% can be achieved with an overall thickness of below 100 nm and sheet resistance of 5 Ω/sq. This is considered a step forward because single-layer ITO electrodes of 400-nm thickness to have the same sheet resistance (Guillén and Herrero, 2011). Although multilayer TCOs have successfully shown a reduction in ITO consumption, they do have flaws, namely that the layers of the TCO must be very thin to have the desired transmittance (Liu et al., 2010). When the layers of a TCO are very thin, it will suffer from a non-uniform surface that can affect its electrical properties (Liu et al., 2010).

Progress in TCO development continues as researches have begun to introduce dopants into the main TCO material to tweak the performance. Through the doping of materials, defects like oxygen deficiency are introduced into the structure, which allows conductivity in the TCO itself. However, not all materials can be doped in order to give a good conductivity that is suitable for some applications. Timothy et al. (1999) mentioned that the In in In_2O_3 can be substituted by Sn to yield a conductive, n-type sn-doped In_2O_3, while some other materials like Al_2O_3 can be doped efficiently. As such, this brings forth an opportunity to find a combination of material and dopant that will produce a material that fulfils the requirements of an ideal TCO.

2.1. Mechanism of TCO and its role in various applications

TCOs play different roles in devices, and in some devices they are an important component. An application of TCOs is in organic light emitting devices (OLEDs) for flat panel displays or as a light source. In an OLED, the TCO layer serves as the anode that collects electrons flowing from the electron source cathode and in which holes are injected by the hole-injection layer. The efficiency of an OLED device can be improved by selection of the proper electrode material. Besides having high transparency and low resistivity, material with a high work function tends to aid in the hole-injection efficiency (Tsujimura, 2012). Fig. 1 shows the typical OLED structure.

In thin film technology of solar cells, the TCO plays a role quite similar to an OLED; that is, it acts as a transparent anode. In most solar cells, the material currently used is ITO or FTO. Even though FTO is becoming more widely preferred in solar cell researches, it does have a drawback: although it has high transmittance, its resistivity is still quite high. Therefore, solar cells need to have additional current collectors sealed from the dyes by a sealant to reduce the resistivity, especially in larger sized solar cells.