論 文 内 容 の 要 旨

1. Research background

Modern society is directly connected with the development of digital and information technology. While about 70% of all everyday information is perceived through vision. In addition, during the worldwide pandemic of the COVID-19, interaction and remote working have increased and become massively ubiquitous. All these attributes of daily activity are inevitably associated with displays interaction, which have become an integral part of our lives. Current trends in the technology of flat panel display (FPD) are aimed at improving the image quality, increasing the refresh rate of the displayed image, increasing the resolution, the creation of flexible devices and so-called "transparent electronics". However, the development of next-generation displays requires improvements in the performance of the thin-film transistors (TFTs) that drive the individual image pixels, and make up the active control matrix of the liquid crystal display (LCD). Ultimately, it is clear that the development of semiconductor materials that can meet the requirements of future FPD parameters is a key goal. From the beginning of the 2000s, both amorphous and polycrystalline oxide semiconductors (OS) have been shown to be promising candidates to replace amorphous silicon technology. Owing better properties, including high mobility of over 10 cm2/Vs, high transparency, and room temperature synthesis. Currently, there is a need to further improve the OS based TFT mobility.

Since the unique structure of OS consists of a large spatial overlap of metal s-orbitals without a pronounced directionality, forming the bottom of the conduction band (CBM), while the top of valence band (VBM) is formed by oxygen p-orbitals, which ensures their high transparency. However, OS synthesis is always accompanied by the formation of various high-density defects due to oxygen deficiency. Thus, we propose a method of synthesizing OS in a hydrogen-containing atmosphere, which is one of the ways to control the electrical properties, as well as a way to passivate defects improving the device characteristics. Nevertheless, despite the fact that H is the most common impurity, its role and influence in each particular case can vary significantly. This fact requires further study and comprehensive analysis, while the mechanism in each specific case still remains without proper explanation.

In this study, in order to improve electrical properties of the p- and n-type OS, the effects of H doping in OS for TFT application were studied. The H adding effect was investigated in the three following topics: 1) Hydrogen doping effect in polycrystalline SnOx for p-type conductivity TFT; 2) Defect passivation and carrier reduction mechanisms in hydrogen doped n-type In-Ga-Zn-O (IGZO:H) films upon low-temperature annealing for flexible device applications; 3) Hydrogenated polycrystalline n-type In-Ga-O (IGO:H) for high-mobility TFTs.

2. Structure of the dissertation

The purpose of this dissertation is to study the effects of H doping to improve the electrical properties of OSs, to establish the mechanism of H influence in p- and n-type OS, and to determine the positive and negative effects of H addition both on the properties of thin films and on the characteristics of devices. This thesis is organized as follows through the 5 chapters.

Chapter 1 - Introduction

As a background of this dissertation, the main directions of the development of FPD technology are reviewed. The main stages and history of the OS development are considered. Key features, structure and characteristics, advantages and disadvantages of both polycrystalline and amorphous OS are summarized and presented, as well as the main trends in the development and their device applications. The focus of the chapter is on the role and effect of H in OS. The main known effects, including change in electrical properties, passivation of defects, and improvement of device performance and what role H plays are discussed.

Chapter 2 – Development and analysis of the SnO_x material for p- type channel TFT

This chapter describes the research of OS with p-type conductivity based on tin oxide (SnO_x) for TFT application. Most of the OS materials are those with n-type conductivity. However, p-type materials development is important because achieving high performance p-type oxide TFTs will promote a new era for electronics in rigid and flexible substrates. In addition, it will allow the production of complementary metal-oxide-semiconductor (CMOS) logic devices and make possible use of highly compact circuits with low power consumption.

Optimization and development of a reference synthesis process for obtaining the films with p-type conductivity is presented. Both the comprehensive analysis of thin-film properties and the fabrication of TFTs confirming the nature of p-type conductivity were performed. A basic optimal process window was developed, which is very narrow and limited to control due to the rapid and easy oxidation of Sn in oxygen-excess condition and the instability of SnO at temperature of 250 OC. In order to optimize and improve the characteristics of both the thin-films and TFT, we focused on the H doping to SnO_x films. The effects of different H ratios on the change of optical, structural, electrical properties, chemical composition, and TFT performance were investigated. Both the positive and negative effects of H doped SnO_x films were found. Thus, it was found that H doping resulted in the change of the initial Sn/SnO/SnO_2 phase composition. Initial metal content in the film decreased by 3% suggesting additional formation of tin vacancies (V_{Sn}) and V_{Sn}- H complexes, resulting in increased concentration of holes. In addition, the SnO_x films deposition in H containing atmosphere leads to oxygen vacancy (V_O) termination by H. This substitution results in formation of Sn- H^+ bonds, which leads to slight increase in Hall mobility of holes after annealing because of reduction of carrier traps. Thus, the H doping can be used as one of the ways to improve the characteristics of p-type TFT.

Chapter 3 – Defect passivation and carrier reduction mechanisms in hydrogen doped In-Ga-Zn-O (IGZO:H) films upon low-temperature annealing for flexible device applications

Research results of the H adding effect on the n-type IGZO film properties, and mechanism causing the activation temperature reduction are presented.

Synthesis of IGZO films is always accompanied by the formation of various defects. These defects affect not only the film properties, but also the TFT performance. Therefore, they should be properly mitigated during post-processing in order to achieve quality films and high performance devices. The most common treatment method for IGZO is post-deposition annealing at 300 °C. However, this temperature is not suitable for flexible or wearable electronics applications, whose processing temperature is limited due to polymer substrate utilization. This limitation requires the development of new approaches which will allow to achieve the comparable electrical properties at relatively low-temperature. Low-temperature activation process is a key approach for OS materials utilization in flexible and wearable electronics. We reported that H adding during the IGZO deposition reduces the activation temperature to 150 °C, demonstrating a strong potential of this method. However, the mechanism upon H adding causing low-temperature activation has not been clarified in details. In this chapter, we focused on the mechanism of the H adding during the IGZO films synthesis resulting in the carrier density control and defects passivation after low-temperature activation. Thus, it was found the higher the H content the greater the O diffusion and the larger the shift of the diffusion starting temperature toward a lower temperature. Diffusion starting temperature shifted from 190 °C to 90 °C toward higher H content due to the induced structural change facilitating the O diffusion. HAXPES analysis revealed the near Fermi level defect reduction for H doped IGZO films after the 150° C annealing. These results demonstrate that H introduction into the IGZO films holds promise for low-temperature applications, such as flexible electronics.

Chapter 4 – Hydrogenated polycrystalline n-type In-Ga-O (IGO:H) for high-mobility TFTs

In this chapter the properties of hydrogenated polycrystalline (poly) n-type In-Ga-O films are discussed. The results of thin films analysis and the effects on TFT characteristics both during IGO channel formation and during device fabrication are presented.

According to recent reports, active research in further increasing the mobility of the OS TFTs is focused on the use of materials with high-In content (In-rich). Thus, the mobility of monocrystalline In2O3 has been reported of 160 cm2/Vs, which makes polycrystalline InOx a potential candidate material for high-mobility TFT application. However, such materials tend to be polycrystalline due to their ease of crystallization at low temperature, as well as spontaneous crystallization even during room temperature deposition. In addition, the electron concentration in In-rich OS is high, about 1020 cm-3, which requires the development of methods to reduce the electron concentration for application in TFTs.

It was reported that the transparent conductive oxide (TCO) of polycrystalline InOx can be formed by solid-phase crystallization at 200° C by a sputtering process in the H2O vapour contained Ar and O2 atmosphere. In this study we investigated the H doping effects on electrical and structural properties of the IGO film. It was found that intensive H doping suppressed the crystallization during the film deposition. Hydrogen incorporation into the IGO film reduced the electron concentration by two orders of magnitude from 1020 cm-3 to below 1018 cm-3 through crystallization process. On the other hand, the unintentional H doping can also occur in subsequent TFT fabrication steps.

Therefore, the formation of a passivation layer is necessary to protect the channel and ensure TFT reliability. However, H can diffuse into the TFT channel, both during the passivation layer deposition and from it on later stage. Thus, film properties and influence of H originated from the related processes are investigated. In addition, the film properties in relation with TFT performance are discussed.

Chapter 5 – Conclusion and future work

The results of the research are summarized and the steps for further research are listed in this chapter.