Doctoral thesis/dissertation Digest Form

Title of Doctoral Thesis: Low-Temperature Solution Combustion Synthesis of Tin Oxide Thin-Film Transistors for Low-voltage Device Applications (低電圧デバイス応用に向けたスズ酸化物薄膜トランジスタの低温溶液燃焼合成)

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(Summary)

The development of high-performance transistors and electronic devices has become highly significant in response to the escalating demand for next-generation display technologies. The current trend is toward flexible, bendable, and transparent transistors for next-generation displays, sensors, and integrated circuits. In the field of thin-film transistors (TFTs), amorphous oxide semiconductors (AOS) are a class of semiconductors that have gained significant popularity in recent years due to their exceptional performance, which surpasses that of a-Si and poly-Si. Despite the developments in indium-oxide-based TFTs, sustainability and safety issues drive the investigation of other metal oxides. Owing to their availability and low toxicity, tin oxide (SnO_2) is gaining attention as an alternative to indium oxide. Both oxides possess similar electronic properties with high intrinsic mobility. However, SnO_2 TFTs often have highly negative on-voltages and large subthreshold swings due to intrinsic defects that make the carrier concentration modulation difficult.

This work focuses on the challenges associated with solution-processed tin oxide TFTs and proposes a promising solution involving the use of the solution combustion synthesis (SCS) technique. SCS is a solution processing technique that uses the heat released by combustion to help the formation of more M-O-M networks in the film. Aside from obtaining excellent M-O networks due to the heat provided by the exothermic combustion reaction, the trigger temperature needed to start the combustion is significantly lower than most sol-gel methods. This dissertation has the following objectives (1) investigate the effect of using SCS compared to conventional sol-gel in the fabrication of Si_xSn_yO films and TFTs (2) enhance the standard SCS process by using a bifunctional oxidizer that can remove chloride impurities, and (3) develop an SCS-derived aluminum oxide thin-film with excellent dielectric strength for applications on

low-voltage Si_xSn_yO TFTs.

By using SCS, we were able to improve tin oxide-based TFTs in three different aspects. First, compared to the conventional sol-gel method, a better metal oxide (M-O) network was formed in the tin oxide thin film, which enhanced the conduction path of mobile carriers, allowing better mobility and higher drain current for the TFT. Secondly, SCS facilitated the reduction of impurities that are detrimental to the quality of the semiconductor material. These impurities include chlorine and carbon which are derived from the precursor. As confirmed by XPS, the M-O bond increased while the oxygen vacancies decreased. In addition, we varied the oxidizer-to-fuel ratio to optimize the SCS films. The optimum oxidizer-to-fuel ratio was 1:3, producing a film with a roughness of 0.38 nm. We also determined the optimum Sn concentration for fabricating Si_xSn_yO TFTs. Optimized Si_xSn_yO TFT with 0.10M Sn concentration has a linear mobility of 3.14 cm^2/Vs, *SS* of 2.49 V/dec, I_{ON}/I_{OFF} of 10^4, and V_{ON} of -29.5 V.

Despite the improved TFT performance using SCS, the tin oxide TFT still suffers from problems caused by precursor-related impurities such as high *SS* and highly negative V_{ON} . Thus, we developed a novel route of eliminating chloride ions by using $AgNO_3$ that acted as both oxidizer and chloride remover via precipitation with silver. This breakthrough is very significant because we were able to greatly improve the significant properties of the TFT such as subthreshold swing and turn-on voltage. After using the improved SCS method, the *SS* dramatically decreased from 2.91 V/dec to 0.32 V/dec. Improvement in the *SS* is explained by the reduction of chloride ions and a decrease in oxygen vacancies in the Si_xSn_yO film. The highest mobility value (1.92 cm^2/Vs) is obtained using 0.25 M Sn concentration. The mechanism of mobility improvement as higher Sn molarity is used is explained by the increase in M-O bonds and film thickness. Furthermore, we confirmed that the Sn^{4+}/Sn^{2+} ratio is vastly affected by the chloride removal and enhanced the n-type semiconductor properties of the TFT. Finally, we were able to expand the SCS technique in the fabrication of a solution-processed oxide gate insulator, which is aluminum oxide. By optimizing the Al_2O_3 thickness and annealing environment, a good breakdown field strength was achieved at 5.6 MV/cm. The optimum $AgNO_3$ thickness is 29.6 nm, and the best annealing environment is 80% N_2 and 20% O_2 environment. By using SCS for both semiconductor and gate insulators, the TFT hysteresis was vastly improved due to the reduction of interface defects. In addition, the leakage current is largely decreased to $\approx 10^2$ pA and the hysteresis value decreased from 2.1 V to 0.6 V.

In summary, this work was able to vastly improve tin oxide TFTs by employing a solution combustion synthesis technique, especially in terms of better *SS*, V_{ON}, and hysteresis. Compared to the sol-gel method, a better M-O network and fewer C impurities were obtained using SCS. We also enhanced SCS by using a bifunctional oxidizer that removes chloride impurities. By using an SCS-assisted high-*k* dielectric, low-voltage TFT was also achieved with further optimizations needed to improve TFT performance. Overall, we can confirm that SCS is a highly efficient and adaptable method to create superior-quality metal oxide networks at much lower temperatures than traditional techniques.