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Development of spinel-type $ZnGa_2O_4$ thin-film transistor and its application to flexible devices

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Abstract

To solve the chemical and electrical issues of amorphous oxide semiconductors, a $ZnGa_2O_4$ thin-film transistor (TFT) having a spinel-type crystal structure was developed. It was observed that this material is insoluble even at pH 1 and has high durability to bias stress. In addition, we developed a pH sensor as an application destination utilizing its characteristics and demonstrated its potential.

1. Introduction

Recently, the development of a roll-to-roll system has progressed as a manufacturing technique with higher throughput and lower cost in the field of electronics. In film formation technology in particular, roll-to-roll (R2R) coating equipment has been developed in vapor deposition, sputtering, and chemical vapor deposition methods and contributes to many product fields.

On the contrary, although there are plate printing methods and ink-jet methods for patterning thin films formed by R2R equipment, it is difficult to obtain high resolution and high overlay accuracy while maintaining high throughput. Therefore, there are several issues with manufacturing advanced semiconductor devices with the R2R process. Last year, Nikon reported on R2R type exposure equipment. [1] This exposure equipment can expose a flexible substrate such as a film with high resolution and high overlay accuracy with high throughput as compared with the printing method. With the popularization of this R2R film coating equipment and patterning equipment, it is expected to not only lower cost by improving productivity but also new electronic devices making full use of flexibility will be proposed. In the future, we expect to create novel needs and added value in electronics devices. In this paper, we introduce a new oxide semiconductor that can be expected to be applied to flexible devices. Various composition developments of oxide semiconductors, typified by amorphous InGaZnO (IGZO), have been improved with the goal of high mobility and low temperature processing. [2] However, both chemical stability and electrical stability are poor, and there are issues such as insertion of an etch stop layer and performance degradation due to bias stress damage. [3][4] Therefore, we considered more chemically stable materials and hypothesized that stable materials as crystal structure would be both chemically and electrically stable. In addition, we expect that the application can be extended to sensors such as chemically stable pH sensors other than conventional thin-film transistors (TFTs).

In this paper, we focus on $ZnGa_2O_4$ with a spinel-type crystal structure. Although this material has been reported to be fluorescent, it is rarely reported as an oxide semiconductor material. [5] [6] However, its band gap is approximately 4.2 eV; although it is a wide band gap semiconductor material, spinel, which is a crystal structure, has been known to be a stable material for many years. Although the spinel crystal structure is AB_2O_4, the A site and the B site, which are the metal sites in this structure, take a structure surrounded by oxygen and oxygen vacancy rarely occurs. Therefore, it can be expected that the structure will be very chemically stable. We evaluated this material for new device properties and applications such as chemical stability, electrical stress tolerance, and pH sensing.

2. Experiment

The films were grown by sputtering. The substrate temperature was set to 190 °C, the pressure during film formation was set to 0.22 Pa, and Ar + 4% H_2 was prepared for the sputtering gas. As sputtering targets, a target of only ZnO and a sintered target obtained by mixing ZnO and Ga_2O_3 were prepared. Then, stoichiometric $ZnGa_2O_4$ can be obtained by co-sputtering the targets. Figure 1 shows the relationship between the composition ratio of Zn and Ga and x-ray diffraction (XRD) patterns in the obtained samples. The composition ratio of Zn and Ga was determined by x-ray fluorescence spectroscopy (XRF). From these results, when the composition ratio of Zn to Ga in the film is 1:2, only the spinel diffraction pattern is observed. On the other hand, the XRD pattern of ZnO and Ga_2O_3 was confirmed when the composition shifted from 1:2. For this paper, device fabrication was carried out using a composition ratio

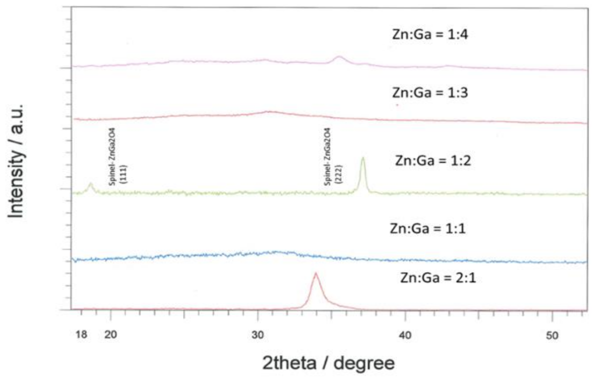

Fig. 1 X-ray diffraction (XRD) results

such that Zn and Ga are 1:2 as the sputtering condition.

Device fabrication was carried out on a thermal oxide Si film (300 nm)/highly doped p-Si substrate, and bottom-gate top-contact structure with Al layer as the source / drain electrode. Electrical device characteristics and bias stress test, some electrochemical measurements were measured with a semiconductor parameter analyzer.

3. Results & Discussion

First, we show the durability of each oxide material to acid. A hydrochloric acid solution adjusted from pH 1 to 7 is dropped onto the various types of oxide semiconductors formed on the Si substrate. After standing for 10 min, it was evaluated whether each thin film was etched. Table 1 shows the pH value when each material is etched. Amorphous IGZO was etched at about pH 3, and indium gallium zinc tin oxide (IGZTO), which is said to have relatively high etching resistance, was also etched at pH 2. However, the spinel-type $ZnGa_2O_4$ is not etched even at pH 1, and it is also highly resistant to alkali. In contrast, since amorphous $ZnGa_2O_4$ was etched at pH 3, it was observed that chemical resistance was improved by crystallization.

Table 1 Relationship between material and etched pH

Material	Crystalline structure	The pH of acid etching solution
$ZnGa_2O_4$	Spinel	< 1
$ZnGa_2O_4$	Amorphous	3
IGZO	Amorphous	3
IGZTO	Amorphous	2
ZnO	Wurtzite	4
ITO	Bixbyite	4

Subsequently, the result of the bias stress test is shown in Fig. 2. The device structure was formed on a Si wafer, and an amorphous IGZO-TFT was prepared for comparison. To compare materials, the process temperature was set to 190 °C each, and all devices were formed without introducing a passivation layer. We noticed that spinel-type $ZnGa_2O_4$ has almost no Vth shift in either positive bias stress tests or negative bias stress tests. In other words, it was found that the chemically stable structure is electrically stable.

Finally, a pH sensor was prototyped using this spinel material. In the future, we are hoping for application to flexible and disposable sensors, and we hope to directly detect acids and alkalis of various concentrations by taking advantage of high chemical durability. In this device structure, a reservoir was formed on a spinel-type $ZnGa_2O_4$ -TFT, and a solution of pH 1, 7, 14 was dropped thereon. In the measurement, the potential difference (ΔVgs) between the gate electrode and the solution for each pH level was measured. Based on the potential difference at pH 7, no damage of the device occurred at pH 1 or pH 14, and it was possible to measure accurately. It was observed that the

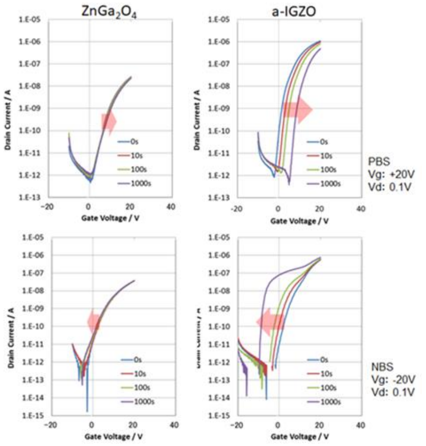

Fig.2 The results of positive bias stress (PBS) and negative bias stress (NBS) testing

relationship between pH and the measured potential difference was approximately 30 mV/pH, indicating that it is possible to measure in a wide pH range.

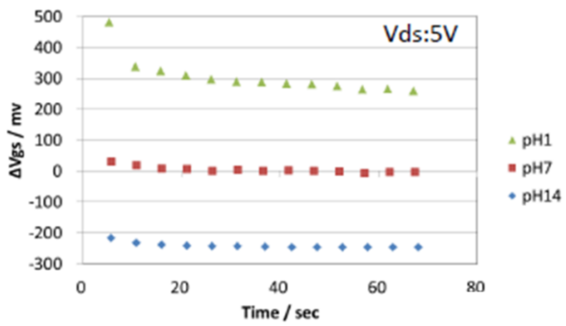

Fig. 3 The result of the potential difference of the gate voltage at pH 1, 7, and 14

4. Conclusions

It was confirmed that a chemically and electrically stable device can be formed by synthesizing spinel-type $ZnGa_2O_4$. Chemical durability results demonstrated that it is insoluble even at pH 1 to 14, and etching resistance is higher than any oxide semiconductor. It was confirmed that it is robust against electrical device stress, so it is considered that there is a strong correlation between chemical durability and electrical stability. In addition, a prototype pH sensor utilizing these characteristics was developed and will be applied to flexible sensors in the future.

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