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LaF_3 electrolyte-insulator-semiconductor sensor for detecting fluoride ions

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ABSTRACT

Electrolyte-insulator-semiconductor (EIS) sensor is commonly considered for chemical and biosensing applications due to its small size and simple fabrication method. Here, we demonstrate a fluoride-sensitive EIS sensor using thermally-deposited polycrystalline lanthanum fluoride (poly LaF_3) film as sensing membrane, which is cheaper than single-crystal LaF_3. The sensing characteristics are analyzed for poly LaF_3 layers deposited at different temperatures, and the EIS sensors with the sensing membrane formed at 500 °C exhibit excellent sensing response to fluoride ions with a high sensitivity of 52.3 mV/pF and low limit of detection of 1.9 ppb. This limit of detection is lower than previously reported values in the literatures. In addition, the poly LaF_3 film deposited at 500 °C has good stability with a low hysteresis voltage of 5.1 mV and a small drift rate of 0.67 mV/h. These superior metrics come from a rather well crystallized LaF_3 structure including denser surface grains, enhanced preferential crystalline (002) plane, and improved stoichiometric composition. Furthermore, the sensors show a good selectivity over other ions such as NO_3^- and SO_4^{2-}.

1. Introduction

Monitoring fluoride concentration is important in biomedical applications, environmental monitoring, and many industrial processes such as aluminum, glass, and plastic manufacturing. Fluoride ions (F^-) can affect cellular metabolism and induce health problems like hypocalcemia [1]. Fluoride ion-sensitive electrode (FISE) with single-crystal lanthanum fluoride (LaF_3), which was introduced by Frat and Ross in 1966, has been widely used for detecting F^- due to its good selectivity, potential stability, and fast response [2,3]. However, the FISE is too bulky for hand-held measurement systems; in addition, the single-crystal LaF_3 is not economical due to its high cost [4]. These features limit extension to portable and disposable types of systems, which are popular in the era of internet of things (IoT). Several alternatives such as an ion-sensitive field-effect transistor (ISFET) [5–7], an electrolyte-insulator-semiconductor (EIS) capacitive sensor [8], and a light-addressable potentiometric sensor (LAPS) [9] have been proposed to overcome the limitations of FISE. They all have similar sensing component of the EIS structure with differences in measurement techniques. The EIS capacitive sensor among them could be well suited for portable and disposable sensor platforms due to several advantages such as simple device structure, small size, and uncomplicated fabrication process. The EIS sensor with LaF_3 can quantify the concentration of F^- in aqueous solutions by measuring the change in capacitance. The selective dissolution of F^- at the surface sites of the LaF_3 film changes the surface potential at the interface between the insulator and electrolyte in proportion to the concentration of F^-, resulting in a shift of the capacitance-voltage (*C-V*) curve [8,10]. Though polycrystalline (poly) LaF_3 film is preferred for low cost sensor platforms, it has exhibited poor sensing characteristics and susceptibility to interference in the past [3]. Moreover, improving the structural and sensing characteristics of the poly LaF_3 film requires complex fabrication methods including a sintering step for 2 h at 1200 °C and long cooling time to avoid thermal shock damage to the sensing layer. The sintering process is not suitable for portable and disposable systems with small size sensors due to high initial costs, large material quantity needed, and difficulty in fabricating nanostructures.

Here, we report a highly sensitive fluoride sensor using the EIS structure with poly LaF_3 as the sensing membrane. The poly LaF_3 film is deposited by thermal evaporation, which is compatible with conventional semiconductor fabrication processes. The effect of substrate temperature T_{sub} on the structural properties (morphology, crystalline structure, and chemical composition) and sensing characteristics (sensitivity (S_{pF}), limit of detection (LOD), hysteresis, and drift rate are investigated by field emission-scanning electron microscope (FE-SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and *C*-

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V measurements. Finally, the selectivity for other anions (NO_3^- and SO_4^{2-}) is tested.

2. Experimental work

2.1. EIS sensor fabrication

The process flow to fabricate the poly LaF_3 EIS sensors is shown in Fig. S1. All devices were fabricated on p-type (100) wafer with a resistivity of 8–12 Ω cm. First, boron ion with a dose of 10^{16} cm^{-2} was implanted on the backside of the wafer to form an ohmic contact, followed by annealing at 1000 °C. Before depositing the poly LaF_3 film, a 5 nm thick SiO_2 was thermally grown as an interfacial layer to improve the interface quality such as low trap density, small stress, and good adhesion [11]. Before evaporation of the poly LaF_3 film, each T_{sub} condition (25, 150, 300, and 500 °C) was maintained for 20 min for sufficient heat transfer to the wafer. The reactor was pumped down to below 1×10^{-6} Torr to minimize the contamination of reaction chamber. Then, a 70 nm thick poly LaF_3 film was thermally evaporated using pure LaF_3 granule (99.995%) at a deposition rate of 2 Å/s. Natural cooling in a high vacuum chamber followed thermal evaporation of the poly LaF_3 film. The back metal electrode (200 nm thick Ag) was deposited using e-beam evaporation. Finally, the device was covered with a 2 µm thick SU-8 photoresist except for the sensing area. Fig. 1 shows the schematic and optical microscopic image of the fabricated EIS sensor. An Ag/AgCl reference electrode (RE) was fabricated using an electrochemical reaction between pure Ag wire (99.99%, diameter: 500 µm, Sigma Aldrich) and 0.1 M potassium chloride (KCl). The voltage fluctuation of the fabricated RE is negligibly small during the ion sensing measurement [7]. The container for the pF solution was formed over the exposed sensing area using epoxy (Devcon) and pipette tip (Eppendorf). All EIS sensors have the same sensing area of 0.2 mm^{-2} and poly LaF_3 thickness of 70 nm (Fig. 1(b) and (c)).

2.2. Structural analysis and electrical measurement

The morphology of the poly LaF_3 films was investigated using FE-SEM (JEOL, JSM 7800F prime) operated under gentle beam mode for high resolution images. In addition, the crystalline structure and chemical composition of the films were examined by XRD (Rigaku, RINT2500V) using CuKα (λ = 0.154 nm, 40 kV/200 mA) and XPS (VG Scientific, ESCALAB 250). All peak positions in the XPS analysis were calibrated by the C_{1S} position at 284 eV. For sensing measurement, fluoride standard ion solution (NaF_3) and total ionic strength adjustment buffer (TISABII) were carefully mixed to make a proper pF solution in the range from pF 2 to pF 8. Sodium nitrate ($NaNO_3$) and sodium sulfate (Na_2SO_4) were also prepared to evaluate the selectivity for other anions (NO_3^- and SO_4^{2-}). The sensing performance of the EIS devices was determined by measuring the *C-V* curves using a LCR meter (Agilent, E4980A) in the dark box and shield room to prevent interference from light and noise. An AC voltage with amplitude of 25 mV and frequency of 1 kHz was applied to the Ag/AgCl reference electrode while the backside electrode was connected to the ground. The flat-band voltage (V_{FB}) is defined at the voltage when the normalized capacitance is 0.5. Three devices in each category of T_{sub} conditions (25, 150, 300 and 500 °C) were used to evaluate sensing performance of the poly LaF_3 sensors.

3. Results and discussion

3.1. Structural properties of the poly LaF_3 film

Fig. 2 shows the top-view and cross-sectional-view SEM images of the poly LaF_3 films revealing columnar microstructures. However, the vertical shape of the columnar microstructures varies slightly depending on the T_{sub}, and the shape variations can be explained by the classical structure zone model (SZM). The SZM describes the film morphology and its dependence on the material properties and deposition temperature. According to the classical SZM, the columnar microstructure of deposited films can be generally classified as a function of T_{sub}/T_m as follows [12,13]:

Zone I: $T_{sub}/T_m \le 0.15$

Zone T: $0.15 < T_{sub}/T_m \le 0.30$

Zone II: $0.30 < T_{sub}/T_m \le 0.50$

Zone III: $0.5 < T_{sub}/T_m$

where T_m is the melting temperature of the films. The reported melting temperature of LaF_3 is 1493 °C [14]. The adatom diffusion is negligible for very low T_{sub} (zone I) values, and the microstructures have tapered units separated by voided growth boundaries. At higher T_{sub} (zone T), the surface diffusion of adatoms becomes significant and orientation selection occurs into the low diffusivity plane during grain growth. This

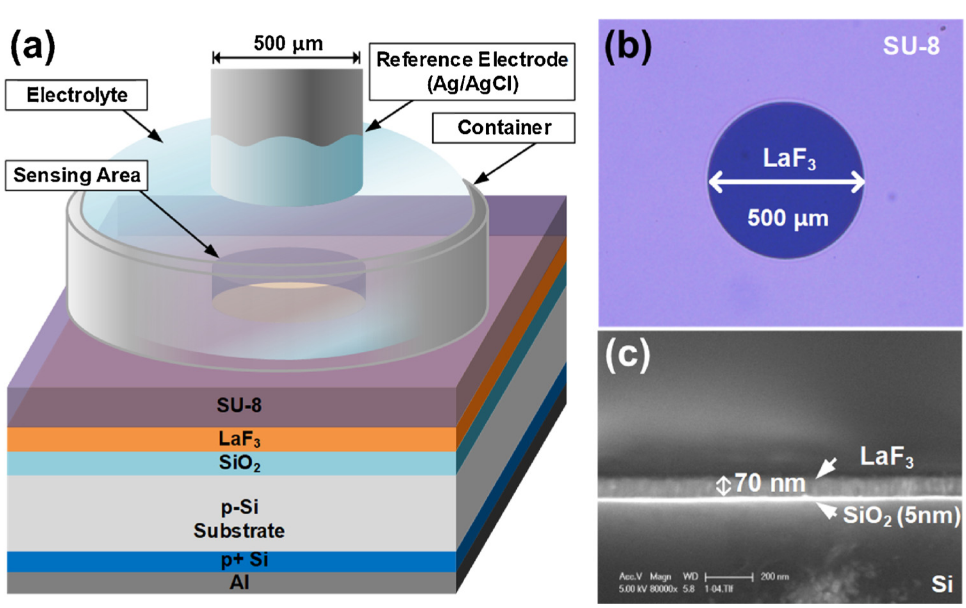

Fig. 1. (a) Schematic diagram, (b) optical microscopic image, and (c) cross-sectional SEM image of the fabricated poly LaF_3 EIS sensor.