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Investigation of Sc_2O_3 Based All-Solid-State EIS Structure for AlGaIn/GaN HEMT pH sensor

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Abstract—In this work, an all-solid-state electrolyte-insulator-semiconductor (EIS) device is developed for pH sensing performance evaluation of insulating materials. The EIS capacitor incorporates scandium oxide (Sc_2O_3) sensing film deposited on undoped gallium nitride (u-GaN) by thermal evaporation. The structural and morphological features of the thin films annealed at different temperature (650-850°C), were investigated through X-ray diffraction and AFM analysis. A gold wire with diameter of 25 μm was bonded on the device and served as the quasi reference electrode for the C-V measurements and pH sensitivity characterizations. After correction of the measured capacitance regarding the pH dependent variation of the standard potential $E^0(\text{pH})$ of gold, the Sc_2O_3 EIS capacitor prepared with an annealing at 650°C exhibited a linear response with a sensitivity of 40 mV/pH while the device with the as-deposited Sc_2O_3 film showed nonlinear behavior and, those annealed at temperature higher than 650°C were shown to be insensitive to pH variation.

Keywords—MIS; EIS; quasi reference electrode; pH sensor; Sc_2O_3 ; undoped GaN.

I. INTRODUCTION

The French project of long-term deep geological disposal of high and medium activity radioactive waste (Cigéo project) involves the use of large volume of cementitious materials embedded in a clayrock. In this context, IRSN, the French public expert in charge of the scientific evaluation of the nuclear and radiological risks, seeks to experimentally evaluate the pH of cementitious materials as a proxy for the aging of concrete structures in contact with clay materials. The diffusive exchange between the two environments could be problematic since it can affect the intrinsic properties of the materials in contact, leading to issues in the durability of the cement-based infrastructures [1]. To monitor and model this exchange, pH measurement of the water trapped in the pores of the concrete is a key point [2]. Conventional pH sensors (glass electrode [3]) cannot be used in such a harsh environment. Therefore, with the aim of long-term monitoring of storage facilities, we propose to use AlGaIn/GaN-based HEMT (High Electron Mobility Transistor) sensors (see Fig. 1, with functionalized gate) which have been shown to be able to handle harsh conditions [4,5]. Such devices can be also grown on top of h-BN layer

allowing their lift-off and report on other substrate to improve their performance [6].

This kind of sensor, called ion sensitive field effect transistors (ISFETs) is being increasingly used for detection of ionic activity in various application fields such as chemistry, medicine, biology, etc. An ISFET structure is a modified Metal-Oxide-Semiconductor Field-Effect Transistor (MOSFET) whose metal gate is replaced by an electrolyte solution to be tested and an external reference electrode which provides the electrical connection [7-10]. This device which was first demonstrated by Piet Bergveld in 1970 [7] has the advantage to combine both the sensing and the transducing functions into one small and rapid device with CMOS system integration compatibility in multiple ion sensors.

To fabricate these devices, silicon and its oxide have traditionally been used because of their outstanding performance, availability and ease of manufacturing. This kind of materials cannot unfortunately handle harsh environment. Heterostructures and quantum structures including III-V and II-VI compounds semiconductors have also demonstrated interest in various types of chemical-sensing devices for biochemical processes [11-14]. For the gate functionalization, several metal oxides such as Si_3N_4 , Al_2O_3 , ZrO_2 , HfO_2 , Ta_2O_5 ... [15-18] have been extensively studied, but most of them degrade when exposed to strong alkaline medium. In contrary, scandium oxide (Sc_2O_3), with a band gap of 6.3 eV and dielectric constant of 14, unlike other metal oxides, is compatible with strongly alkaline medium like cementitious materials. Furthermore, ISFET with glass reference electrode has been already demonstrated [13,15,18].

This work aims to investigate pH sensitivity of a Sc_2O_3 /u-GaN based EIS and MIS devices (see Fig. 1), in order to optimize the growth and annealing parameters of the Sc_2O_3 layer, which will be then deposited on top of AlGaIn/GaN HEMT transistor gate, to form AlGaIn/GaN-based ISFET [3,17] with on chip integrated quasi reference electrode (instead of conventional fragile glass electrode).

The paper presents the fabrication process of a simple and combined EIS/MIS capacitor using Sc_2O_3 and u-GaN, as well as the C-V (pH) measurement set up and sensitivity

extraction, using a non-conventional reference electrode, with the possibility to measure small volumes of electrolyte. The evolution of sensitivity to hydrogen ions (in the pH range of interest 7-13) as a function of postdeposition annealing temperature is discussed based on structural and morphological (X-ray diffraction and atomic force microscopy) analysis coupled with measured I-V curves.

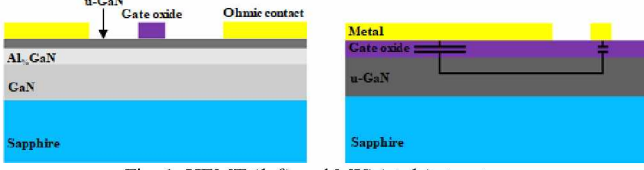


Fig. 1: HEMT (left) and MIS (right) structures.

II. EXPERIMENTAL

A. Growth and device fabrication

A 3.5 μm -thick undoped GaN was grown by MOCVD (Metal Organic Chemical Vapor Deposition) on a sapphire substrate. The details about u-GaN layer growth conditions can be found in [20]. Prior to Sc_2O_3 deposition, u-GaN layer was solvent-cleaned and HF treated. Then thermal evaporation was carried out using 99.99% pure Sc_2O_3 pellets (Kurt J. Lesker). 20 nm-thick Sc_2O_3 was deposited at substrate temperature of 200°C. Then, a one hour-postdeposition annealing (PDA) at different temperatures (650°C, 750°C and 850°C) in N_2 atmosphere was realized, for comparison with the as-deposited film. The fabrication procedure of MIS and EIS structures includes the materials growth, metallization after photolithography, PDMS (polydimethylsiloxane) coating and localized openings using biopsy punch (for electrical contact and formation of a reservoir for EIS characterizations). A Au/Ti (100/10 nm) bilayer was deposited by e-beam evaporator for metallization. The last step of the fabrication is gold wire (with diameter of 25 μm) bonding between two Au/Ti contacts located in two different reservoirs. Instead of the usual deposition of metal on the backside of the semiconductor substrate, a large capacitive virtual ground contact (Au/Ti) around the MIS gate contact and EIS reservoir [19] has been used. The ground contact was made large enough so that its capacitance is much higher than the one of the MIS and EIS capacitors to study. The operation principle of the EIS structure lies in the flat-band voltage dependence on the surface potential at the insulator-electrolyte interface. This flat-band voltage for an ISFET or EIS device is [15]:

$$V_{\text{FB}} = E_{\text{ref}} - \psi_0 + \chi_{\text{sol}} - \Phi_s/q - (Q_{\text{ox}} + Q_{\text{ss}})/C_{\text{ox}} \quad (1)$$

where E_{ref} is the potential of the reference electrode, ψ_0 is the pH-dependent surface potential, χ_{sol} is the surface dipole potential of the solution, Φ_s is the work function of the electrons in the semiconductor, q is the elementary charge, Q_{ox} is the charge located in the oxide, Q_{ss} is the charge located on the surface and interface, and C_{ox} is the gate oxide capacitance.

B. Structural and electrical characterizations

The crystallinity of the different Sc_2O_3 films were analyzed using high-resolution X-ray diffraction (HRXRD) in Panalytical X'pert Pro MRD system with Cu K α radiation in triple axis mode. The surface morphology and roughness have been analyzed by AFM. Fig. 2 shows the electrical characterization setup for MIS and EIS capacitors. A Keysight E4990A impedance analyzer was used for C-V measurement. The applied small ac signal was 10kHz/50mV. Commercial pH buffer solutions (with pH 7, 10, 11, 12 and 13) were used to evaluate the sensitivity of the EIS sensor.

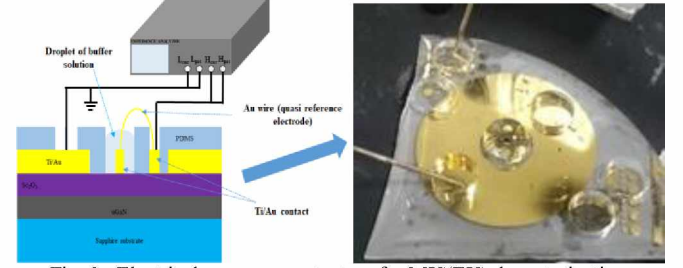


Fig. 2 : Electrical measurement set up for MIS/EIS characterization.

III. RESULTS AND DISCUSSION

The results of XRD analysis are presented on Fig. 3. From the 2θ - ω scan recorded in the range 10° to 70°, only the peak corresponding to the Sc_2O_3 (211) plane can be seen for all the films (annealed and as-deposited). The intensity of the peak increases and its FWHM decreases when the annealing temperature is increased. Also, the 2θ position of the peak is shifted towards higher values when the annealing temperature is increased. These results point out the effect of annealing on the crystallographic features (lattice parameter, crystallite size and microstrain) and indicates a better crystallinity for Sc_2O_3 films annealed at 750°C and 850°C.

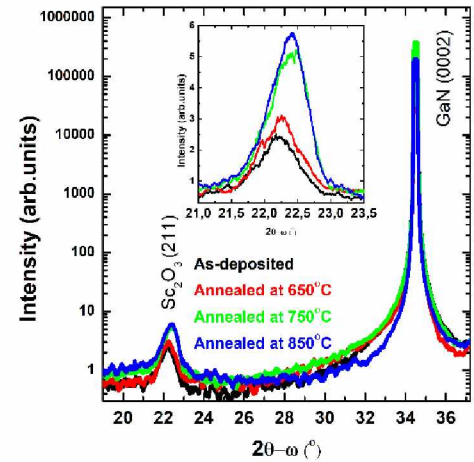


Fig. 3: XRD spectra of Sc_2O_3 films annealed at different temperatures.

Figure 4 shows the surface morphology of the Sc_2O_3 films obtained by AFM analysis. The films annealed at 750°C and 850°C are clearly granular with similar roughness of 1.4 nm and 1.3 nm respectively. The as-deposited film does not show a typical surface morphology (relatively smooth but not flat)

and has a roughness of 0.6 nm. The film annealed at 650°C has a very flat surface with roughness as low as 0.2 nm.

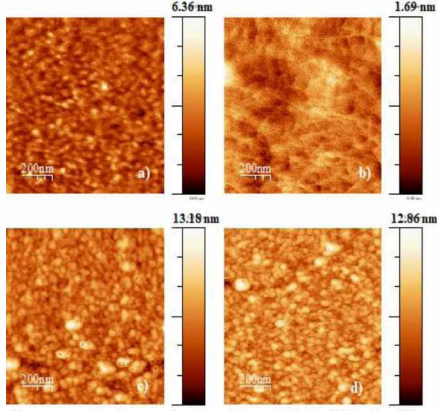


Fig. 4: Surface morphology obtained by AFM of Sc_2O_3 films annealed at different temperatures: a) as-deposited, b) 650°C, c) 750°C, d) 850°C.

Fig. 5 shows the measured C-V curves for the Sc_2O_3 films annealed at 650°C and 850°C, and their dependence with pH. Films annealed at 850°C (and 750°C not shown here) are non-sensitive to pH. The as-deposited film (not shown here) has been shown to exhibit some sensitivity but with a nonlinear behavior. Only the 650°C-annealed film has been shown to have a linear sensitivity to pH.

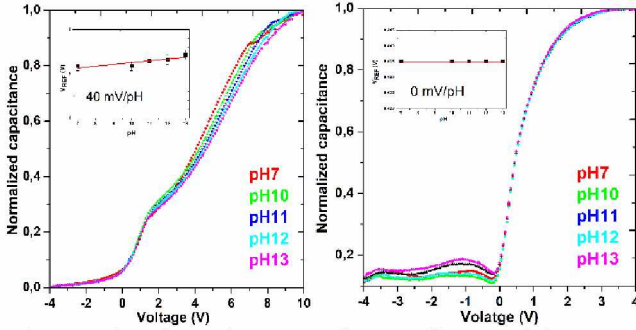


Fig. 5: pH dependence of C-V curves for Sc_2O_3 films annealed at 650°C (left) and 850°C (right).

Unlike the conventional reference electrode such as Ag/AgCl electrode which has a constant potential regardless the variation of pH, the potential of the quasi reference electrode varies as a function of pH. Considering the pH-dependence of the standard potential of Au micro wire (the quasi reference electrode), the sensitivity value was corrected by weighting the measured potentials at 0.5 of the normalized C-V curves, with the respective values of the standard potential $E^0(\text{pH})$ of Au for a given pH. These standard potentials were obtained by linear interpolation from the theoretical data at $\text{pH}=0$ and $\text{pH}=14$ reported in the literature [22, 23]. The correction is made based on the principle of the potential which is effectively applied to the EIS capacitor, according to the distribution of voltage across the measurement circuit. After correction, a sensitivity of 40 mV/pH is obtained for the EIS capacitor with the 650°C-annealed Sc_2O_3 film. Fig. 6 shows the measured I-V curves of the MIS capacitors. For all the MIS capacitors, the current density is lower in the positive voltage range. This can be attributed to the formation of a depletion region when the positive voltage is added [24].

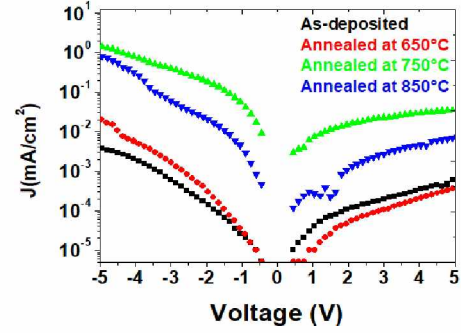


Fig. 6: I-V curves measured on the MIS capacitors.

The current density increases with the increase of the annealing temperature except for the film annealed at 650°C. This result is consistent with the fact that the grain boundaries (as shown in Fig. 4) which are leakage channels [24], increase with the annealing temperature except for the sample annealed at 650°C which does not show a grain structure. In the light of the whole results, it seems that the pH sensitivity is closely related to the level of insulation and/or surface morphology of the dielectric material.

These set of data show that the best sensitivity is obtained for the dielectric material with the lowest leakage current corresponding to the flattest morphology. However, this is not enough to explain the peculiarity of the pH-insensitivity of some of the EIS sensors. Further investigation is needed to understand this. The pH-sensitivity in EIS structures being governed by the mechanisms of surface ion adsorption and charge modulation at the oxide-semiconductor interface, surface and interface chemical composition as well as interface states analysis of the capacitors would be relevant. The understanding of this insensitivity using metal oxides could be an advantage for the development of high quality and stable REFETs. Furthermore, by optimizing the annealing temperature, time and atmosphere, the Nernstian (59.2 mV/pH) or even super-Nernstian pH sensitivity may be reached with our thermal evaporated Sc_2O_3 on u-GaN.

IV. CONCLUSION

A study of Sc_2O_3 -based all-solid-state EIS structure was presented. Sc_2O_3 films annealed at 650°C in N_2 for one hour were shown to exhibit a linear sensitivity of 40 mV/pH. This performance may be optimized by adjusting further the annealing parameters. Also, non-conventional MIS/EIS structure is shown to be suitable for rapid investigation of sensitive insulating materials.

The next step will be the integration of the optimized Sc_2O_3 layer on top of AlGaN/GaN HEMT transistor gate, to form AlGaN/GaN-based ISFET with on chip integrated quasi reference electrode.

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