Materials Science in Semiconductor Processing 71 (2017) 217–225

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Influence of CuS membrane annealing time on the sensitivity of EGFET pH sensor

Fayroz A. Sabah[a,b,*], Naser M. Ahmed[a,**], Z. Hassan[c], Munirah Abdullah Almessiere[d]

[a] School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
[b] Department of Electrical Engineering, College of Engineering, Al-Mustansiriya University, Baghdad, Iraq
[c] Institute of Nano Optoelectronics Research and Technology (INOR), Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
[d] Physics Department, College of Science, University of Dammam, Saudi Arabia

ARTICLE INFO

Keywords:
CuS membrane
EGFET
PH sensitivity
Hysteresis
Annealing time

ABSTRACT

In this study, CuS membranes were deposited on glass substrates using spray pyrolysis, and then annealed at 150 °C for durations of 5, 15 and 30 min. The precursor materials for the synthesis of the CuS membranes include copper chloride and sodium thiosulfate dissolved in deionized water. 0.4 M concentration of the mixed solution was subsequently sprayed on the glass substrates at 200 °C. Afterwards, the as-deposit membranes were implemented as extended gate field effect transistors (EGFET) for pH sensors. The structure, morphology, resistance, sensitivity and linearity of the membranes were determined. The structural characteristics showed that the maximum average grain size of the CuS membrane was 24.2 nm after 30 min of annealing. The sensitivity of the membranes was measured in buffer solutions of pH 2, 4, 6, 8, 10 and 12. The sensitivity increased with annealing time until maximum values of 31.5 μA/pH and 27.8 mV/pH were attained at 30 min, with minimum resistance of 400 Ω and minimum hysteresis of 11.4 mV. Thus, the ideal annealing time for optimum sensitivity, resistance and hysteresis is 30 min.

1. Introduction

The search for a less-complex, rapid and cost-effective analytical tests that use very low concentrations of chemical compounds has attracted immense attention in the manufacture of electrochemical sensors [1]. For example, biosensors based on pH sensing are extensively used in the production of medical instruments, and ion sensitive field-effect transistors (ISFETs) were developed based on the metal oxide field effect transistor (MOSFET) to improve sensitivity. Since Bergveld [2] first utilized the field-effect transistor for neurophysiological measurements in 1970, several kinds of chemical-sensing electrodes have exploited ISFETs. There are also numerous publications on the behaviour of chemical-sensing electrode devices [3]. ISFET is more advantageous than conventional glass electrodes because of its small size, rapid response, high input impedance, low output impedance and applicability as a biochemical sensor [4]. The development of ISFET is similar to that of commercial MOSFET, although ISFET has its metal gate electrode detached in order to expose the underlying insulator layer to the solution. Based on ISFET, Van Der Spiegel et al. [5] developed a different structure referred to as extended gate field effect transistor (EGFET), which is cost-effective, requires less-complex packaging with a relatively more flexible shape and simpler structure compared to ISFET [6]. The EGFET also provides higher long-term stability, given that the ions from the chemical environment are prevented from any possible interaction with the FET gate insulator. The EGFET consists of two parts: sensing membrane and conventional MOSFET. The sensing membrane of pH-ISFET and pH-EGFET is typically a high sheet resistant metal oxide, although that of pH-EGFET is a highly conductive material to enable the unimpeded transmission of electric signals [6].

The Gouy-Chapman-Stern-Grahame (CGSG) or site-binding model [7] has been effectively used to model and merge electrokinetic surface potential measurements of inorganic oxides (a group of numerous diverse effects that arise in heterogeneous fluids, or in porous bodies occupied with fluid, or in a rapid flow over a even surface) with surface charge data obtained from titration experiments. In this model, core amphoteric ionizable groups of the oxide surface develop a net charge in reaction to the solution concentration of potential ions or pH. In addition, the model also enables the specific adsorption of anions and cations of the supporting electrolyte at the Stern plane. Thus, the modelling of both electrokinetic and titration data entails the combination of recognition of the ionisation of intrinsic surface groups and of

* Corresponding author at: School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia.
** Corresponding author.
E-mail addresses: fayroz_arif@yahoo.com (F.A. Sabah), naser@usm.my (N.M. Ahmed).

http://dx.doi.org/10.1016/j.mssp.2017.07.001
Received 9 April 2017; Received in revised form 29 May 2017; Accepted 1 July 2017
1369-8001/

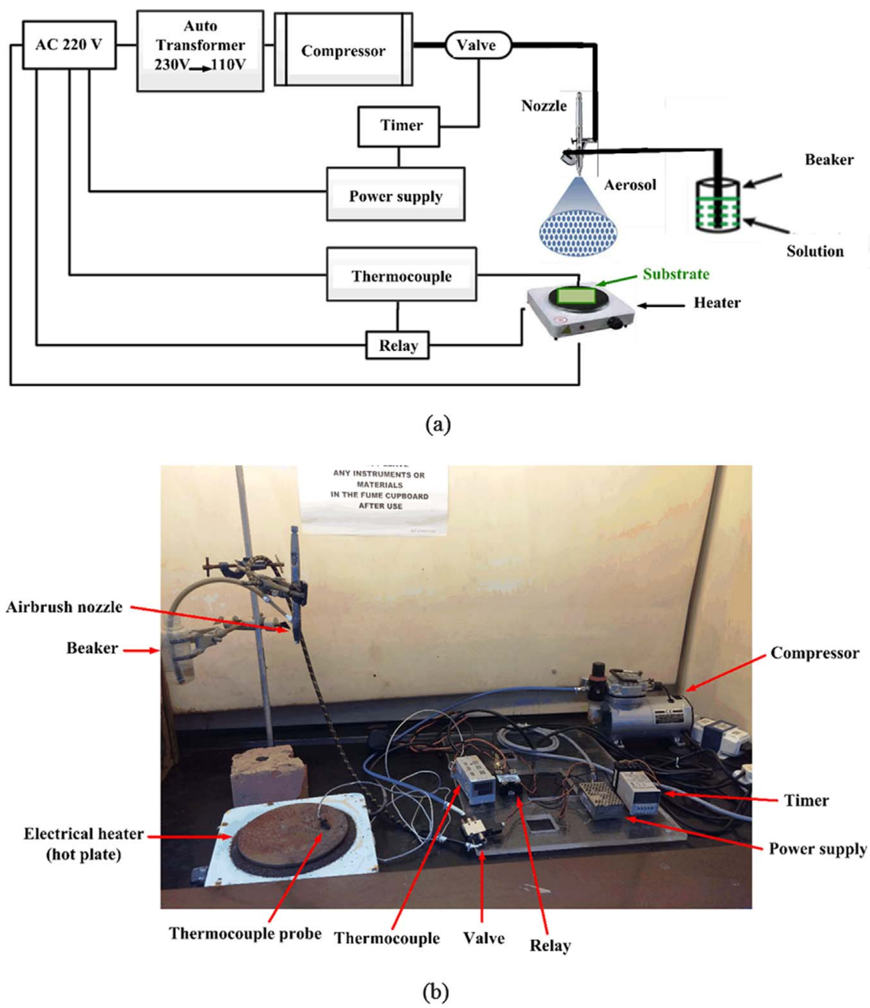

Fig. 1. Spray pyrolysis deposition setup (a) schematic (b) image.

ion binding in the CGSG model [8].

CuS is considered a good semiconductor material for pH sensor, because of its high electrical conductivity, inexpensiveness, availability in bulk, single crystal, and thin film forms related to its structural and electrical properties. In general, these characteristics are controlled by the local chemical structure (stoichiometry) of CuS, which is highly dependent on the preparation method and conditions of deposition that dominate during growth [9]. An additional benefit of CuS is its ability to be easily synthesized using several deposition techniques. Ziqing Xu et al. [10] examined aptamer-CuS/GO/Glu composites, which were prepared through non-covalent intercalation and π-π stacking. Their findings are essential to the development of multifunctional drug-delivery systems for highly effective treatment against tumor cells. Jie Sun et al. [11] synthesized light-sensitive core@shell CuS@PNIPAM-g-CS nanocomposites via the temperature-tunable copolymerization of NIPAM and CS in the presence of CuS NCs. They found that the nanocomposites achieved a light-triggered release of dual drugs at the same time and improved chem-photothermal synergistic therapy for in vitro treatment of cancer cells.

In this study, CuS membrane was deposited using spray pyrolysis deposition (SPD). The method has been extensively reported in literature [12–16] due to its ability to synthesize uniform and dense films with preferred crystallinity over several spraying cycles. SPD also has the capability to create whole multilayer devices by means of successive deposition of different layers in the same chamber that possesses combinations of properties. The SPD technique also ensures CuS film adhesion on the substrate is achieved, as many other techniques failed to provide good adhesion with the films slipping from the substrate. On the other hand, the technique has some limitations regarding the control of temperature. Nonetheless, the striking balance between the simplicity of the SPD equipment and the wide range of plausible implementations of the respective products makes the spray pyrolysis method a versatile technique. The ability to execute several processes with the same device fabricated by spray pyrolysis increases its production efficiency, and reduces the operation time [17]. The as-deposit membranes have been annealed at 150 °C for durations of 5, 15 and 30 min, with the membrane annealed for 30 min showing the highest sensitivity and minimum resistance. Sabah et al. [18–21] studied the influence of light illumination and darkness, MOSFET, film thickness and substrate type on the pH sensing characteristics of CuS membranes. Previous related studies [18–21] revealed that the pH sensitivity of CuS is highest values in the dark, in the presence of MOSFET, with low membrane thickness and on the glass substrate. However, there is no study on the annealing of CuS membrane applied as a pH sensor. This is the first time the effect of CuS membrane annealing on the pH sensing characteristics was studied in this work. This study suggests that annealing time affects the growth and conductivity of CuS membrane, thus influencing pH sensing behaviour. Moreover, this study is the first to discuss the influence of heat on the CuS membrane as well as the conductivity and application of annealed CuS membrane as a pH sensor. As reported in literature, CuS membrane annealed at 150 °C for 30 min provides the best sensitivity characteristics among all other CuS membranes.