Sensors and Actuators B 205 (2014) 143–150

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A gold/organic semiconductor diode for ppm-level humidity sensing

Faramarz Hossein-Babaei*, Pejman Shabani

Electronic Materials Laboratory, Industrial Control Center of Excellence, Electrical Engineering Department, K. N. Toosi University of Technology, Tehran 16315-1355, Iran

ARTICLE INFO

Article history:
Received 4 April 2014
Received in revised form 4 August 2014
Accepted 20 August 2014
Available online 27 August 2014

Keywords:
Humidity sensor
H_2O adsorption
Gold nanolayer
Organic semiconductor
MEH-PPV
Hydrophobicity

ABSTRACT

The cooperative electric field of surface-adsorbed polar organic molecules has been shown to control charge transport in adjacent solid layers or interfaces. While the adsorption of water monomers on different metal surfaces has also been extensively investigated, the electronic implications of the mechanism have not yet been explored. Here, we show that H_2O molecules, selectively adsorbed on a ~10 nm-thick gold layer deposited on a hydrophobic semiconductor, substantially change the electron distribution in the gold layer, affecting the electron energy profile at the gold/semiconductor interface and altering the current–voltage characteristics of the structure. This concept is used for the fabrication of a resistive humidity sensor for ppm-level hygrometry. Made by depositing gold nanolayers on an air-stable hydrophobic organic semiconductor, oxidized poly[2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV), the device demonstrates high sensitivity at H_2O concentrations as low as ~1 ppm in air, vacuum and inert backgrounds. The presence of gases such as CO_2 and H_2 in substantial concentrations and oxygen partial pressure variations in air do not interfere with the sensing process. Unlike common Kelvin condensation-based resistive humidity sensors, the electrical resistance of the presented device increases upon exposure to humid atmospheres.

1. Introduction

While detecting many volatile substances at ppm-level concentrations is facilitated by various commercially available sensors, humidity sensing below ~100 ppm (relative humidity 0.4% at 298 K) is still a notorious technical problem [1–3]. Studies on the adsorption of polar organic molecules on metal and semiconductor surfaces [4–8] have shown that the cooperative electric field [5,9] of such surface-adsorbed molecules can control charge transport in adjacent solid layers or interfaces [5–9]. While the adsorption of water monomers on different metal surfaces has also been extensively investigated [10–23], the mechanism has not yet been considered for electronic applications.

Today, the molecular perspective of a water monomer adsorbed on a noble metal surface is fully conceptualized [10,15–18]. Recent findings show that the interaction takes place between the $1b_1$ molecular orbital of the H_2O molecule and the metal surface, which transfixes the molecule close to the surface with its intrinsic electric dipole standing almost parallel to the surface plane [10,17,18]. The asymmetric configuration of this covalent bond transfers a net negative charge from the molecule to the metal atom [11,17]. On a gold (1 1 1) surface, for instance, this covalent bonding holds the H_2O molecule at a distance of 3.05 Å from the surface with its intrinsic dipole moment oriented at an angle of 13° to the metallic surface [7,14], and transfers approximately one tenth of an electron to the nearest gold surface atom [14].

It has been shown that neither the parallel and nor the normal component of the intrinsic dipole of a surface adsorbed H_2O molecule can affect the electrostatic equilibrium condition in the metal a few atomic layers away from the adsorption site [15]. Here, we show that the dipole moment resulting from the asymmetric adsorption bond is roughly of the same magnitude as the intrinsic dipole and is oriented almost normal to the surface plane. The selective arrangement of these dipoles on the surface of a gold layer alters the mobile electron distribution within the layer's cross-section, which can be sensed at a nearby gold/semiconductor interface. The device whose fabrication and operational characteristics are described here utilizes this concept for the electronic determination of the H_2O concentration in the surrounding

---

* Corresponding author. Tel.: +98 21 8873 4172; fax: +98 21 8876 8289.
E-mail addresses: fhbabaei@kntu.ac.ir, fhbabaei@yahoo.com (F. Hossein-Babaei), P_shabani@ee.kntu.ac.ir (P. Shabani).

http://dx.doi.org/10.1016/j.snb.2014.08.061
0925-4005/

atmosphere by evaluating the number of the water monomers adsorbed per unit area of a gold nanolayer.

2. Theory

Upon exposure to a humid atmosphere, a layer of gold deposited on a hydrophobic substrate adsorbs H_2O molecules selectively on its top surface. The hydrophobicity of the substrate ensures this spatial selectivity on a large-area jagged gold layer as the hydrophobic force, stretching out from the substrate surface to considerable distances in atomic scale [24], would protect metal edges at the layer's openings and micro-cracks and would prevent H_2O molecules from diffusing to the metal/substrate interface (Fig. 1a). At low humidity levels, the coverage of the gold surface with the adsorbed molecules, θ, is determined through the Langmuir gas adsorption isotherm [25]. At 298 K, these calculations, given as Appendix A, result in a simple relationship between θ and H_2O concentration in the surrounding atmosphere:

$$\theta = \frac{C}{C+\kappa} \tag{1}$$

wherein C is the water concentration in ppm, and κ is a constant. For the different gold layers deposited by flash-evaporation of gold in vacuum (see below), κ was experimentally determined at 298 K to be within the 250 to 350 ppm range. Assuming the surface density of the adsorption sites equal to that of the surface atoms, the number of H_2O molecules on a unit area of the substrate is obtained from (1):

$$N = \frac{A_{eff}}{A}\frac{\theta}{a_o^2} = \frac{A_{eff}}{Aa_o^2}\frac{C}{C+\kappa} \quad (\mathrm{m}^{-2}) \tag{2}$$

wherein a_o is the diameter of the surface metal ions and A_{eff} is the effective outer (top) gold surface on A (m^2) of the substrate.

The charge redistribution in the cross-section of a thin gold layer, resulting from the selective adsorption of water monomers on its top surface, is determined through the standard electrostatic calculations (refer to Appendix B). The results indicate an increase of Δn in the electron density from its thermal equilibrium level, n_o, within the metal beyond a nanometer below the surface (Fig. 1b). The effect is more profound in thinner metal layers with rough surfaces (Fig. 1b). The total density-of-state function around the Fermi energy level (E_F) in gold [26] translates Δn into a change in E_F which is as much as ΔE_F in magnitude. The plots of ΔE_F against N for gold layers of different thicknesses, produced based on the calculations given in Appendix C, indicate the occurrence of more profound ΔE_F in thinner metal layers (Fig. 1c, dashed lines). The relationship between ΔE_F and C, also presented in Fig. 1c (solid lines), is, then, determined through (2) and the relationship between ΔE_F and N. At 298 K, the predicted ΔE_F for a rough ($A_{eff}/A = 250$) 10 nm-thick gold layer at equilibrium in air containing 5 ppm of H_2O is ~5 meV. Conversely, it should be possible to measure the humidity level in the surrounding atmosphere by an experimental evaluation of ΔE_F.

The predictions of the presented theory are verified by the results of the experiments carried out in different conditions on the devices fabricated (see below). Of course, other types of interactions between H_2O molecules and a gold surface there might exist (such as those conceivable between the electric dipoles interacting electrostatically with the conductive plane with no charge exchange), but the predictions based on these assumptions hardly describe the observed change in the electronic status of the device in response to its exposure to ppm-level humid atmospheres. Indeed, all experimental observations regarding the humidity sensitivity of our device are described by the above given theory which is based on the modern understanding of the H_2O-gold surface interactions described in Section 1.

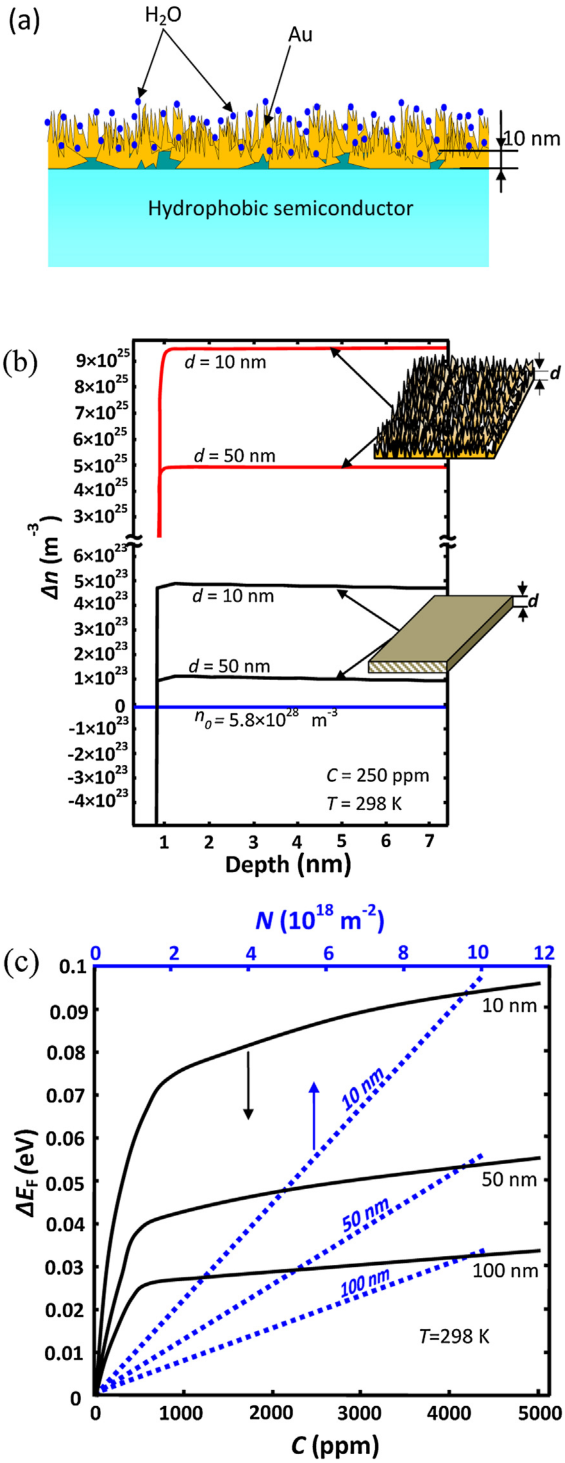

Fig. 1. (a) Schematic presentation of the H_2O molecules adsorbed selectively at the rough top surface of a jagged gold nanolayer deposited on a hydrophobic substrate. The hydrophobicity of the substrate prevents H_2O molecules from diffusing to the metal/substrate interface. (b) The predicted electron population change in the cross-section of the gold layer; much higher electron density alterations are predicted for thinner layers with rough surfaces. (c) The predicted departure of the Fermi level from its intrinsic level plotted vs. the surface densities of the adsorbed water monomers (dashed lines) and vs. the H_2O concentration in the surrounding atmosphere (solid lines).